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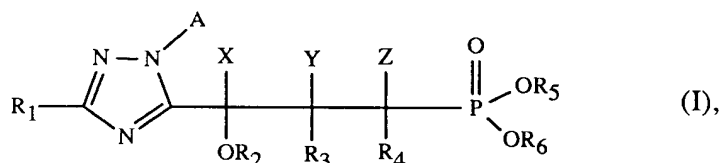
Applicant : **Japat Ltd**
Klybeckstrasse 141
CH-4057 Basel (CH)

Inventor : **Hayakawa, Kenji, Dr.**
1-11-4-1213, Sakasedai
Takarazuka-shi, Hyogo (JP)
Inventor : **Mori, Ichiro, Dr.**
18-31-803, Higashiashiya-cho
Ashiya-shi, Hyogo (JP)
Inventor : **Iwasaki, Genji, Dr.**
1-8-25-103, Mukoyama-cho
Takarazuka-shi, Hyogo (JP)
Inventor : **Matsunaga, Shin-ichiro**
1-1-4-104, Higashinaniwa-cho
Amagasaki-shi, Hyogo (JP)

Representative : **Schluep, Hans-Peter et al**
c/o CIBA GEIGY AG Patentabteilung Postfach
CH-4002 Basel (CH)

Novel triazoles.

A triazole of the formula I



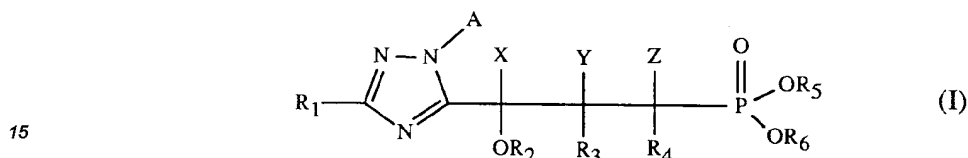
in which the meanings of the radicals are described in claim 1, have a herbicidal and plant-growth regulating action. They are suitable as active substances in weed killers and in compositions for positively influencing the growth of crop plants.

The present invention relates to novel triazoles which have a herbicidal action and are plant-growth-regulating, to processes for their preparation, to compositions containing them as active substances, and to their use for controlling weeds, especially selectively in crops, or for regulating and inhibiting plant growth.

Triazole compounds which have a herbicidal action are generally known. For example, European Patent Application No. 0 078 613 describes herbicidally active triazole compounds.

It has been found that compounds of the formula (I) have a herbicidal and plant-growth-regulating action. They are therefore suitable as active substances in weed killers and in compositions for positively influencing the growth of crop plants.

The triazoles according to the invention are those of the formula I



in which

A is hydrogen, C₁-C₄-alkyl, C₁-C₄-alkenyl, triphenylmethyl, benzyl, a group

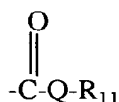


or C₁-C₄-alkyl substituted by hydroxy or C₁-C₄-alkoxy,;

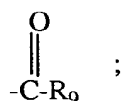
t is 4 or 5;

R₁ is hydrogen, fluorine or C₁-C₄-alkyl;

R₂ is hydrogen, a group



or a group



R₃ is hydrogen or C₁-C₄-alkyl;

R₄ is hydrogen or C₁-C₄-alkyl, or R₃ and R₄ together represent a chemical bond;

R₅ is hydrogen, C₁-C₄-alkyl, benzyl or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation;

R₆ is hydrogen, C₁-C₄-alkyl, benzyl or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation;

X is hydrogen, C₁-C₄-alkyl, C₃-C₆-cycloalkyl, C₁-C₄-haloalkyl, C₁-C₄-alkyl substituted by hydroxy or C₁-C₄-alkyl substituted by -OR₁₄;

Y is hydrogen or C₁-C₄-alkyl or together with X a -CH₂-(CH₂)_p-CH₂- group or together with Z a C₁-C₄-alkylene bridge which is substituted by R₇ and R₈;

Z is hydrogen or C₁-C₄-alkyl or together with X a C₂-C₄-alkylene bridge which is substituted by R₇ and R₈;

Q is oxygen, sulfur or NR₁₀;

R₇ is hydrogen, C₁-C₄-alkoxy or C₁-C₄-alkyl;

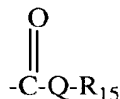
R₈ is hydrogen, C₁-C₄-alkoxy or C₁-C₄-alkyl;

R₉ is C₁-C₆-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl; or C₁-C₆-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl substituted by halogen or C₁-C₄-alkoxy; or phenyl, benzyl; or phenyl, benzyl substituted by C₁-C₄-alkyl, halogen, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, cyano, nitro, C₁-C₄-alkoxycarbonyl or S(O)_m-C₁-C₄-alkyl; or is C₁-C₆-alkoxyalkyl, C₁-C₆-alkylcarbonyloxyalkyl, C₁-C₆-alkoxycarbonylalkyl or C₃-C₆-cycloalkyl;

5 R₁₀ is hydrogen, C₁-C₆-alkyl, C₁-C₆-alkoxy, C₂-C₆-alkenyl, C₃-C₆-alkynyl; or C₁-C₆-alkyl, C₂-C₆-alkenyl, C₃-C₆-alkynyl substituted by halogen or C₁-C₄-alkoxy;

R₁₁ is C₁-C₆-alkyl, C₃-C₆-alkenyl, C₃-C₆-alkynyl; or C₁-C₆-alkyl, C₃-C₆-alkenyl, C₃-C₆-alkynyl substituted by halogen or C₁-C₄-alkoxy; or phenyl, benzyl; or phenyl, benzyl substituted by C₁-C₄-alkyl, halogen, halomethyl, C₁-C₄-alkoxy, cyano, nitro, C₁-C₄-alkoxycarbonyl or S(O)_n-C₁-C₄-alkyl;

10 R₁₄ is hydrogen, a group



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or a group



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R₁₅ is C₁-C₆-alkyl, C₃-C₆-alkenyl, C₃-C₆-alkynyl; or C₁-C₆-alkyl, C₃-C₆-alkenyl, C₃-C₆-alkynyl substituted by halogen or C₁-C₄-alkoxy; or phenyl, benzyl; or phenyl, benzyl substituted by C₁-C₄-alkyl, halogen, halomethyl, C₁-C₄-alkoxy, cyano, nitro, C₁-C₄-alkoxycarbonyl or S(O)_n-C₁-C₄-alkyl;

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R₁₆ is C₁-C₆-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl; or C₁-C₆-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl substituted by halogen or C₁-C₄-alkoxy; or phenyl, benzyl; or phenyl, benzyl substituted by C₁-C₄-alkyl, halogen, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, cyano, nitro, C₁-C₄-alkoxycarbonyl or S(O)_m-C₁-C₄-alkyl; or is C₁-C₆-alkoxyalkyl, C₁-C₆-alkylcarbonyloxyalkyl, C₁-C₆-alkoxycarbonylalkyl or C₃-C₆-cycloalkyl;

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m is 0, 1 or 2;

n is 0, 1 or 2;

p is 1 or 2;

with the proviso that R₁, R₂, R₃, R₄, X, Y and Z are not simultaneously hydrogen; and if R₁, R₃, R₄, X, Y and Z are simultaneously hydrogen, R₉ is not methyl.

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In the above definitions, halogen is to be understood as being fluorine, chlorine, bromine and iodine, preferably fluorine, chlorine and bromine.

Alkyl is, for example, methyl, ethyl, isopropyl, n-propyl, n-butyl, isobutyl, sec-butyl, tert-butyl and the various isomeric pentyl or hexyl radicals.

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Haloalkyl is, for example, fluoromethyl, difluoromethyl, trifluoromethyl, chloromethyl, dichloromethyl, trichloromethyl, 2,2,2-trifluoroethyl, 2-fluoroethyl, 2-chloroethyl and 2,2,2-trichloroethyl.

Alkoxy is, for example, methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, isobutoxy, sec-butoxy and tert-butoxy; preferably methoxy.

Alkenyl is to be understood as being straight-chain or branched alkenyl, for example vinyl, allyl, methallyl, 1-methylvinyl, but-2-en-1-yl, 3-pentenyl, 2-hexenyl or 3-heptenyl. Alkenyl radicals having a chain length of 2 or 3 carbon atoms are preferred.

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The alkynyl radicals occurring in the definitions of the substituents may be straight-chained or branched, for example ethynyl, propargyl, 3-butylnyl, 1-methylpropargyl, 2-pentylnyl or 2-hexynyl. Ethynyl and propargyl are preferred.

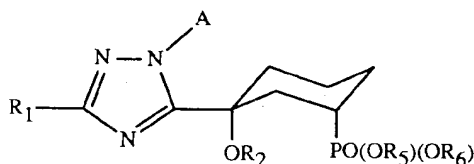
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Alkoxycarbonyl is, for example: methoxycarbonyl, ethoxycarbonyl, n-propoxycarbonyl, isopropoxycarbonyl and n-butoxycarbonyl, preferably methoxycarbonyl and ethoxycarbonyl.

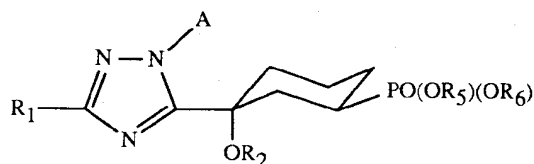
If the compounds of the formula I contain an asymmetric carbon atom, this results in the fact that the compounds can occur in optically isomeric forms. If there is an aliphatic C=C double bond, geometric isomerism can also occur. The formula I therefore also embraces all stereoisomers which are possible and which are in the form of enantiomers, diastereomers or their mixtures.

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For compounds of the formula I, which are cyclic phosphonates, stereoisomers of the following formulae are obtained:



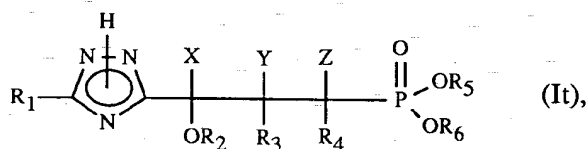
(example for cis-isomer)



(example for trans-isomer)

The configuration of the above mentioned examples of stereoisomers of compounds of the formula I is defined according to the position of the OR₂ group and PO(OR₅)(OR₆) group.

This invention includes all of the tautomeric isomers represented by the following formula of resonance structure:



The term organic ammonium cation is intended to include ammonium cations prepared from low molecular weight amines, that is to say those having a molecular weight below about 300. Examples of such amines include alkylamines, alkenylamines, and alkanolamines containing not more than two amino groups, such as methylamine, ethylamine, n-propylamine, iso-propylamine, the four isomeric butylamines, n-amylamine, iso-amylamine, hexylamine, heptylamine, octylamine, nonylamine, decylamine, pentadecylamine, hexadecylamine, heptadecylamine, octadecylamine, methyl-ethylamine, methyl-isopropylamine, methyl-hexylamine, methyl-nonylamine, methyl-pentadecylamine, methyl-octadecylamine, ethyl-butylamine, ethyl-heptylamine, ethyl-octylamine, hexyl-heptylamine, hexyl-octylamine, dimethylamine, diethylamine, di-n-propylamine, di-iso-propylamine, di-n-butylamine, di-n-amylamine, di-iso-amylamine, dihexylamine, diheptylamine, dioctylamine, ethanolamine, n-propanolamine, iso-propanolamine, N,N-diethylethanolamine, N-ethylpropanolamine, N-butylethanolamine, allylamine, n-butenyl-2-amine, n-pentenyl-2-amine, 2,3-dimethylbutenyl-2-amine, di-butenyl-2-amine, n-hexenyl-2-amine, propylendiamine, diethanolamine, tri-iso-propylamine, tri-n-butylamine, tri-iso-butylamine, tri-sec.-butylamine, tri-n-amylamine, trimethylamine, triethylamine, tripropylamine; heterocyclic amines as, for example, pyridine, chinoline, iso-chinoline, morpholine, piperidine, pyrrolidine, indoline, chinuclidine and azepine; primary arylamines as, for example, aniline, methoxyaniline, ethoxyaniline, o,m,p-toluidine, phenylendiamine, benzidine, naphthylamine and o,m,p-chloroaniline; in particular ethyl-, propyl-, diethyloder triethylamine, preferably iso-propylamine and diethanolamine.

Tetra-substituted ammonium cations are also included, for example tetramethylammonium, tetrabutylammonium, benzyltrimethylammonium, benzyltriethylammonium, tetra-ethylammonium and trimethylethylammonium cations.

Trialkylsulfonium cations include those, for example, in which each of the three alkyl groups, which are not necessary all the same, may contain from 1 to 6 carbon atoms. Trialkylsulfoxonium cations likewise include those in which each of the three alkyl groups, which may be the same or different, may contain from 1 to 6 carbon atoms.

Phosphonium cations include, for example, cations in which the phosphorus atom bears four substituents, each of which may be an alkyl group of one to ten carbon atoms or a phenyl group, for example, the tetrame-

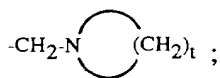
thylphosphonium, tetrabutylphosphonium, and tetraphenylphosphonium cations.

Amidinium cations include, for example, straight chain amidinium cations of formula $R_{14}-C(NH_2)=NH_2^+$, wherein R_{14} is an alkyl radical of, for example, from 1 to 10 carbon atoms, and cyclic amidinium cations such as 1,5-Diazabicyclo[5.4.0]undec-5-ene (DBU).

Alkali metal cations include lithium, sodium and potassium; and alkaline earth metal cations include magnesium, calcium, strontium and barium.

Preferred compounds of the formula I are those, in which

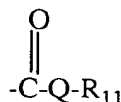
A is hydrogen, C_1 - C_4 -alkyl, triphenylmethyl, benzyl or a group



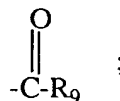
t is 4 or 5;

R_1 is hydrogen, fluorine or C_1 - C_4 -alkyl;

R_2 is hydrogen, a group



or a group



R_3 is hydrogen or C_1 - C_4 -alkyl;

R_4 is hydrogen or C_1 - C_4 -alkyl, or R_3 and R_4 together represent a chemical bond;

R_5 is hydrogen, C_1 - C_4 -alkyl, benzyl or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation;

R_6 is hydrogen, C_1 - C_4 -alkyl, benzyl or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation;

X is hydrogen or C_1 - C_4 -alkyl;

Y is hydrogen or C_1 - C_4 -alkyl or together with X a $-CH_2-(CH_2)_p-CH_2-$ group or together with Z a C_1 - C_4 -alkylene bridge which is substituted by R_7 and R_8 ;

Z is hydrogen or C_1 - C_4 -alkyl or together with X a C_2 - C_4 -alkylene bridge which is substituted by R_7 and R_8 ;

Q is oxygen, sulfur or NR_{10} ;

R_7 is hydrogen, C_1 - C_4 -alkoxy or C_1 - C_4 -alkyl;

R_8 is hydrogen, C_1 - C_4 -alkoxy or C_1 - C_4 -alkyl;

R_9 is C_1 - C_6 -alkyl, C_2 - C_6 -alkenyl, C_2 - C_6 -alkynyl; or C_1 - C_6 -alkyl, C_2 - C_6 -alkenyl, C_2 - C_6 -alkynyl substituted by halogen or C_1 - C_4 -alkoxy; or phenyl, benzyl; or phenyl, benzyl substituted by C_1 - C_4 -alkyl, halogen, C_1 - C_4 -haloalkyl, C_1 - C_4 -alkoxy, cyano, nitro, C_1 - C_4 -alkoxycarbonyl or $S(O)_n$ - C_1 - C_4 -alkyl;

R_{10} is hydrogen, C_1 - C_6 -alkyl, C_1 - C_6 -alkoxy, C_2 - C_6 -alkenyl, C_3 - C_6 -alkynyl; or C_1 - C_6 -alkyl, C_2 - C_6 -alkenyl, C_3 - C_6 -alkynyl substituted by halogen or C_1 - C_4 -alkoxy;

R_{11} is C_1 - C_6 -alkyl, C_3 - C_6 -alkenyl, C_3 - C_6 -alkynyl; or C_1 - C_6 -alkyl, C_3 - C_6 -alkenyl, C_3 - C_6 -alkynyl substituted by halogen or C_1 - C_4 -alkoxy; or phenyl, benzyl; or phenyl, benzyl substituted by C_1 - C_4 -alkyl, halogen, halomethyl, C_1 - C_4 -alkoxy, cyano, nitro, C_1 - C_4 -alkoxycarbonyl or $S(O)_n$ - C_1 - C_4 -alkyl;

m is 0, 1 or 2;

n is 0, 1 or 2;

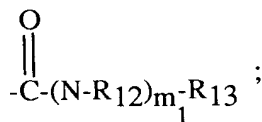
p is 1 or 2;

with the proviso that R_1 , R_2 , R_3 , R_4 , X, Y and Z are not simultaneously hydrogen; and if R_1 , R_3 , R_4 , X, Y and Z are simultaneously hydrogen, R_9 is not methyl.

Further preferred compounds of the formula I are those in which
A is hydrogen, triphenylmethyl, benzyl or a group



R_2 is hydrogen or a group



R_{12} is hydrogen or C_1 - C_4 -alkyl;

m_1 is 0 or 1;

R_{13} is C_1 - C_4 -alkyl, methoxy, trifluoromethyl, phenyl, benzyl, phenyl substituted by halogen or methoxy; or benzyl substituted by halogen, methoxy, methylthio, cyano or trifluoromethyl.

Preferred compounds of the formula I which must be emphasised are those in which A is hydrogen;

R_5 is hydrogen or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation; and

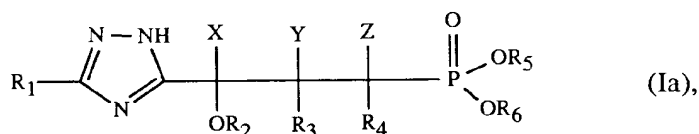
R_6 is hydrogen or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation.

Further preferred compounds from amongst those of the formula I are those in which

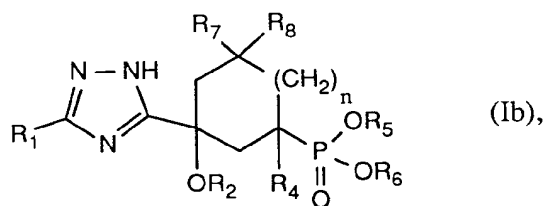
R_1 and A are hydrogen.

Furthermore, compounds amongst those of the formula I which are of particular interest are those in which R_2 and A are hydrogen.

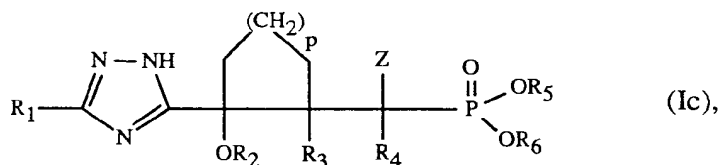
Furthermore, compounds amongst those of the formula I which are preferred are compounds of the formulae



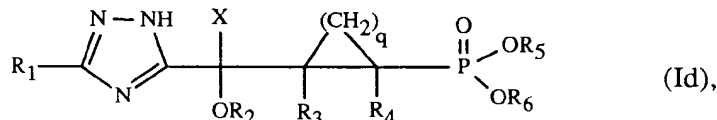
wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , X, Y and Z have the meaning given under formula I, especially preferred are those compounds, wherein R_1 is hydrogen or methyl; R_2 is hydrogen or acetyl; R_3 is hydrogen or methyl; R_4 is hydrogen or methyl; R_5 is hydrogen or ethyl; R_6 is hydrogen or ethyl; X is methyl, ethyl or isopropyl; Y is hydrogen or methyl; and Z is hydrogen, methyl or ethyl;



wherein R_1 , R_2 , R_4 , R_5 , R_6 , R_7 and R_8 have the meaning given under formula I and n is 0, 1 or 2, especially preferred are those compounds, wherein R_1 is hydrogen or methyl; R_2 is hydrogen, acetyl or N-phenyl carbamoyl; n is 0 or 1; R_4 is hydrogen or methyl; R_5 is hydrogen, ethyl or benzyl; R_6 is hydrogen, ethyl or benzyl; R_7 is hydrogen or methyl; and R_8 is hydrogen or methyl;



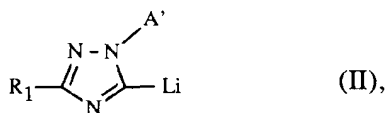
wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , Z and p have the meaning given under formula I, especially preferred are those compounds, wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 and Z each is hydrogen and p is 1 or 2;



wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 and X have the meanings given under formula I and q is 1, 2, 3 or 4, especially preferred are those compounds, wherein R_1 , R_2 , R_3 , R_4 , R_5 and R_6 each is hydrogen; X is hydrogen or methyl; and q is 1, 2, 3 or 4.

From within the scope of the formula I, mention must be made of trans-3-hydroxy-3-(1,2,4-triazole-3-yl)-cyclohexyl-phosphonic acid as a particularly preferred single compound.

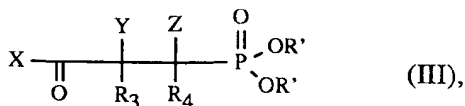
A further subject of the present invention is a process for the preparation of compounds of the formula I which comprises reacting a compound of the formula II



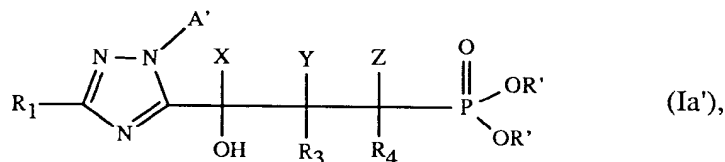
wherein A' is C_1 - C_4 -alkyl, C_1 - C_4 -alkenyl, triphenylmethyl, benzyl, a group



or C_1 - C_4 -alkyl substituted by hydroxy or C_1 - C_4 -alkoxy; and R_1 has the given meaning, with aldehydes or ketones of the formula III



wherein R_3 , R_4 , X , Y and Z have the above given meaning and R' is C_1 - C_4 alkyl or benzyl, with the proviso that R_3 is hydrogen or C_1 - C_4 -alkyl, R_4 is hydrogen or C_1 - C_4 -alkyl, Y is hydrogen or C_1 - C_4 -alkyl, Z is hydrogen or C_1 - C_4 -alkyl, to give a compound of the formula Ia'



wherein A' , R_1 , R_3 , R_4 , R' , X , Y and Z have the given meaning and optionally cleaving protecting groups A'

and/or R' and further converting them into a salt.

Said reaction is carried out in a manner or analogously as given by A.R. Katritzky, Tetrahedron **46** (1990), page 641 ff.

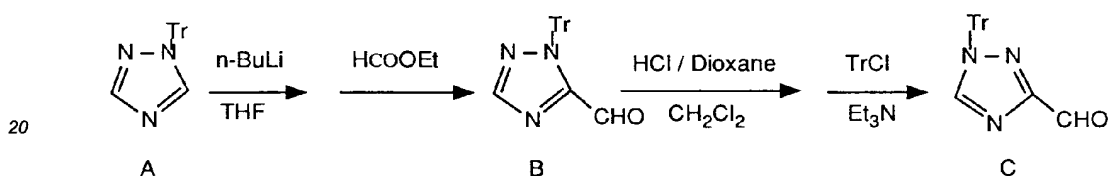
Compounds of formula II are well known and for instance are prepared by reacting a 1,2,4-triazole in an organic solvent, especially tetrahydrofuran or diethylether, in the presence of n-butyl lithium at temperatures between -50 to -90°C.

Compounds of formula III are well known and can for instance be prepared in a manner given in Houben-Weyl, 4th Edition, volume XII/1, pages 463 ff; and Houben-Weyl, 4th Edition, volume E2, pages 352 ff.

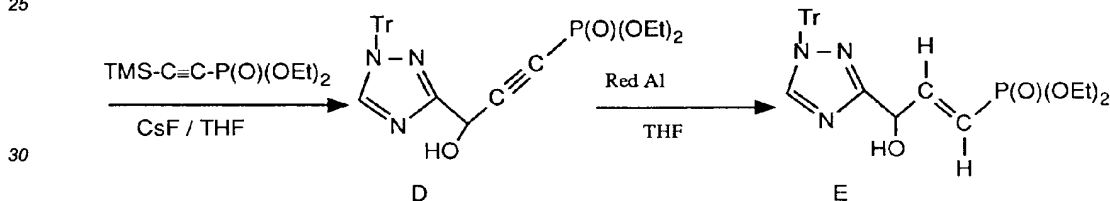
Compounds of the formula I, wherein R₃ and R₄ together represent a chemical bond or Y together with Z represent a C₁-C₄-alkylene bridge can be prepared according to the following reaction schemes ("Tr" is the triphenylmethyl group):

Synthesis of Compound 1.012

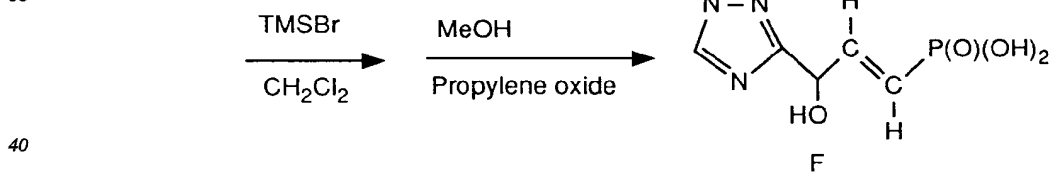
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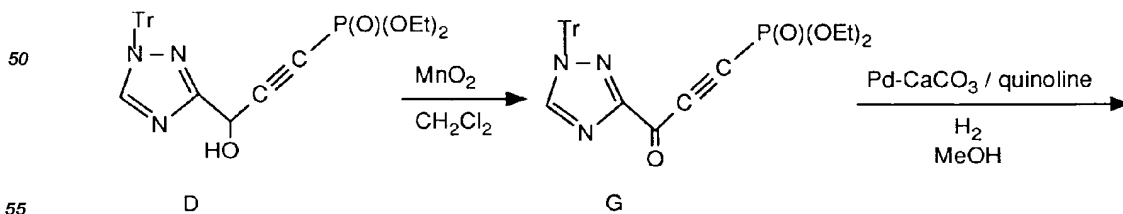
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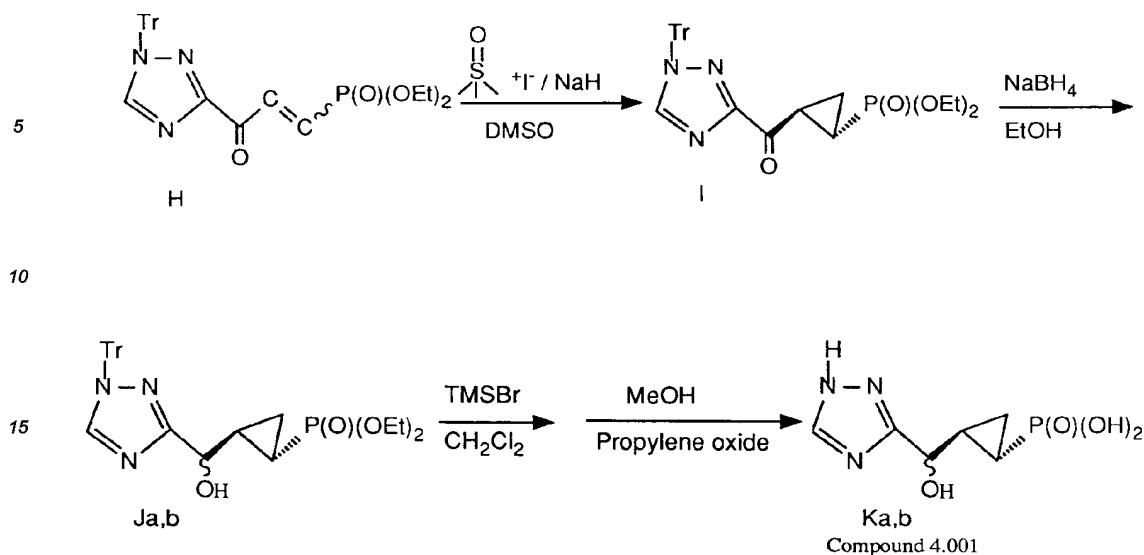


Compound 1.012

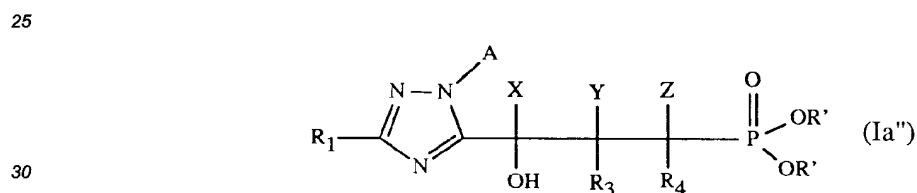
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Synthesis of Compound 4.001

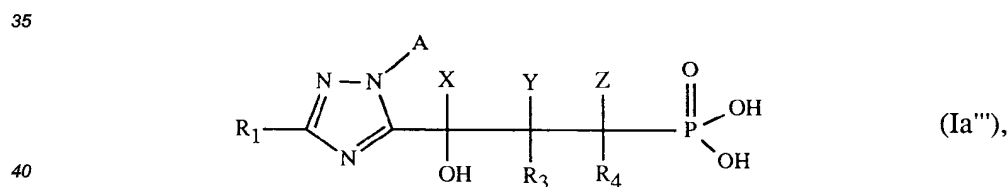




Compounds of formula I, wherein R_5 and R_6 are hydrogen for instance are prepared by treating a compound of formula Ia''



with an acid or a halosilane to obtain a compound of the formula Ia'''



wherein A, R' , R_1 , R_3 , R_4 , X, Y and Z have the meaning given above.

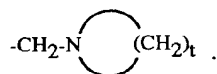
The reaction is carried out in an organic solvent, especially CH_2Cl_2 , at temperatures between 10 and 50°C, especially in a manner or analogously as given by T. Morita, Bull. Chem. Soc. Japan 51 (1978), page 2169 ff.

The protecting groups A as triphenylmethyl, benzyl or a group



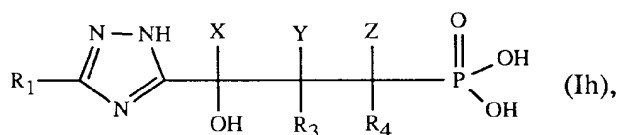
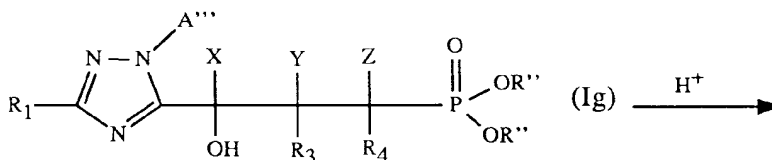
can be cleaved

- 55
- a) under acidic or reductive conditions for the triphenylmethyl group,
 - b) by hydrogenolysis with palladium active charcoal or by reductive cleavage by sodium in liquid ammonia for the benzyl group, or
 - c) by cleavage with $NaBH_4$ for the group



Said reactions are carried out in a manner or analogously as given by D.K. Anderson, *Heterocyclic Chemistry* 23 (1986), pages 1257ff; and A.R. Katritzky, *Tetrahedron* 46 (1990), page 641 ff.

The cleavage of protecting groups for A as triphenylmethyl; R₅ as C₁-C₄-alkyl, benzyl or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation and R₆ as C₁-C₄-alkyl, benzyl or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation can be done sequentially or in a one step process according to the following scheme

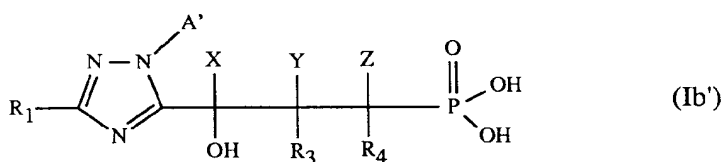


wherein R₁, R₃, R₄, X, Y and Z have the given meaning, A''' is triphenylmethyl and R'' is C₁-C₄-alkyl, benzyl or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation.

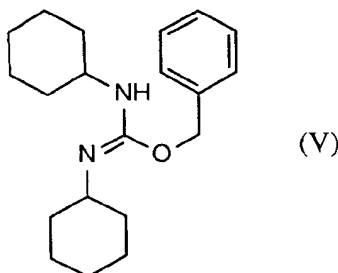
The reaction is carried out without solvent at temperatures between 10 and 50°C in the presence of an organic or inorganic acid, for example HCl or HBr.

Said type of reaction is well known in the art.

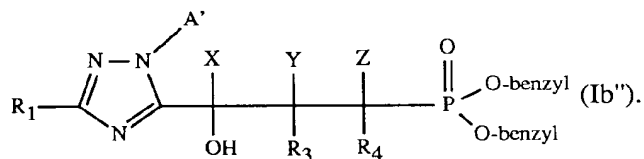
Compounds of the formula I, wherein R₅ and R₆ are benzyl are prepared by reacting the free phosphonic acid compound Ib' with O-benzyl-N,N'-dicyclohexylisourea according to the following scheme



with 2 equivalents of O-benzyl-N,N'-dicyclohexylisourea of the formula



to give the compound of the formula

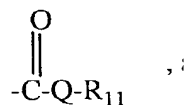


The reaction is carried out under reflux in an organic solvent such as benzene or toluene or dimethylformamide; for example in a manner or analogously as given by M. Hoffmann, *Synthesis* 1988, page 62 ff.

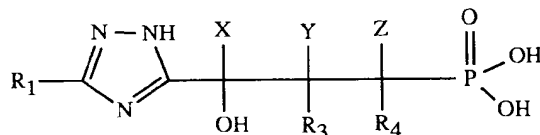
Compounds of the formula I, wherein R₂ is a group



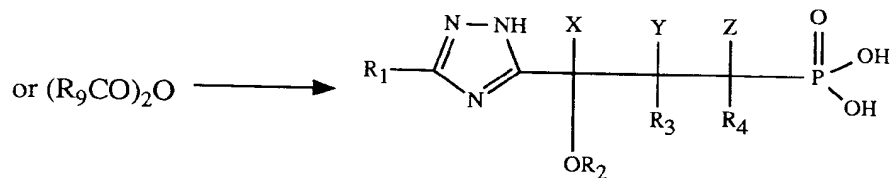
or a group



are prepared by reacting a compound of formula 1h with acid halides or anhydrides according to the following scheme



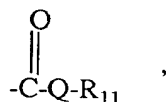
(Ih) + R₉-CO-(halogen, especially chlorine) or R₁₁-Q-CO-(halogen, especially chlorine)



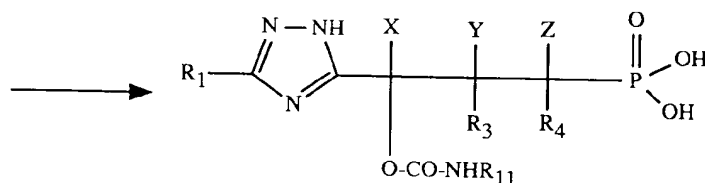
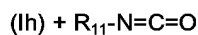
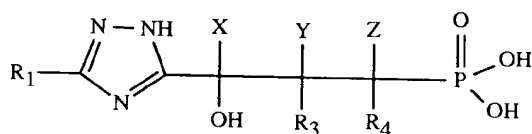
(le), in which R₂ has the meanings given above except for hydrogen.

Said reaction is carried out in a manner or analogously as given in Chem Rev. 1953, 52, pages 237 - 416.

Compounds of the formula I, wherein R₂ is a group



in which Q is NR₁₀ and R₁₀ is hydrogen, are prepared by reacting a compound of formula 1h with isocyanates which lead to carbamates according to the following scheme

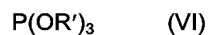


(If).

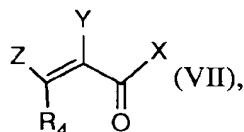
Said reaction is carried out in a manner or analogously as given by Satchell & Satchell, Chem. Soc. Rev, 4, 231 (1975).

1) The ketophosphonates of formula III are prepared

a) by reacting a trialkylphosphite of the formula



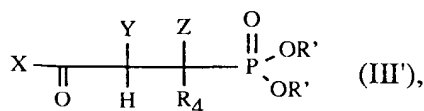
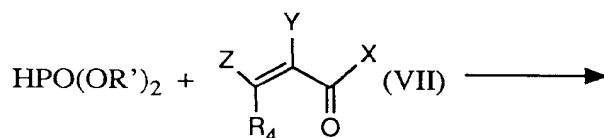
with an enone of the formula



wherein R', Z, R₄, X and Y have the above given meaning.

Said reaction is carried out for example in an organic solvent such as phenol at a temperature between 50 and 100°C, especially in a manner or analogously as given by R.G. Harvey, Tetrahedron, 22 (1966), pages 2561 ff.

b) by addition of a dialkylphosphite to an enone according to the following scheme

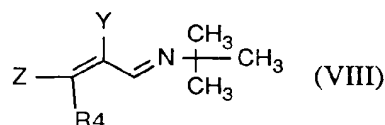


wherein R', R₄, X, Y and Z have the given meaning.

The reaction is carried out in the presence of of an alkoxide, such as sodium ethoxide, at a temperature between 50 and 100°C.

Said reaction can be carried out in a manner or analogously as given by Pudovic, Zhur Obsh. Khim. 27(1957) pages 1617 ff (CA 52, 3713 (1958).

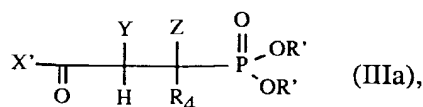
c) by condensation of an aldimine of the formula



with trialkylphosphite of the formula



in the presence of formic acid and after hydrolysis to give compound of formula IIIa

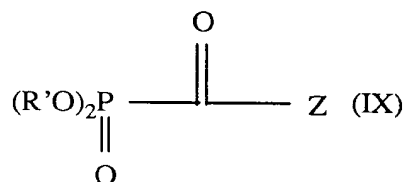


wherein R', R₄, Y and Z have the given meaning and X' is hydrogen.

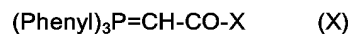
Said reaction is carried out in an alcohol, especially ethyl alcohol at a temperatur between 10 and 50°C in a manner or analogously as given by P. Savignac, Synthesis 1987, pages 1037 ff.

2) Vinylphosphonates of formula XI are prepared by reacting

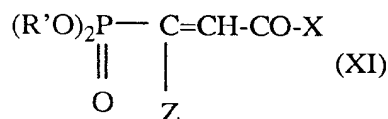
a) an acylphosphonate of the formula



with an enone of formula

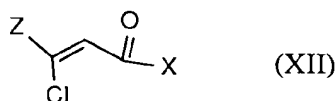


to give a vinylphosphonate of the formula



Said reaction is carried out in an organic solvent, especially in benzene or toluene at a temperatur near the boiling point in a manner or analogously as given by E. Öhler, Monatshefte für Chemie 116(1)(1986), pages 77 ff.

b) β-chloroenones of the formula



with trialkylphosphite of the formula



to give a vinylphosphonate of the formula XI.

Said reaction is carried out without solvent at temperatures between 100 and 150°C in a manner or analogously as given by F. Hammerschmidt, Liebigs Ann. Chem. 1979, pages 492 ff.

Optionally the compounds of formula III, wherein R₃ is hydrogen can be alkylated with an alkylating agent, especially CH₃I or CH₃Br, in the presence of a base, such as lithium diisopropylamide, NaH, tert.-butyl-O⁻K⁺

or DBU (1,8-diazabicyclo[5.4.0.]undec-7-ene) at temperatures between -78 and +50°C according to known alkylating methods, especially alkylation of enamines or silyl enol ethers.

General reviews on 1,2,4-Triazoles are

a) Polya, J.B. in *Comprehensive Heterocyclic Chemistry*, Potts, K.T. Ed.; Pergamon: Oxford, 1984, vol. 5, pages 733 ff.

b) Tempke, C., Jr., *Triazole-1,2,4 in Heterocyclic Compounds*, Montgomery, J.A. Ed.; John Wiley and Sons: New York, 1981; vol. 37.

The compounds of the formula I are employed in unaltered form, as obtainable by the synthesis, or preferably together with the auxiliaries conventionally used in formulation technology, and they are therefore processed in a known manner to give, for example, emulsifiable concentrates, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts, granules, and also encapsulations, for example in polymeric substances. The application methods, such as spraying, atomising, dusting, scattering or pouring, as well as the type of compositions are selected to suit the intended aims and the prevailing circumstances.

The formulations, i.e. the compositions, preparations or combinations comprising the active substance of the formula I and, if desired, one or more solid or liquid additives, are prepared in a known manner, for example by intimately mixing and/or grinding the active substances with extenders, for example with solvents, solid carriers and, if desired, surface-active compounds (surfactants).

The following are possible as solvents: aromatic hydrocarbons, in particular the fractions C₈ to C₁₂, such as mixtures of alkylbenzenes, for example xylene mixtures or alkylated naphthalenes; aliphatic and cycloaliphatic hydrocarbons such as paraffins, cyclohexane or tetrahydronaphthalene; alcohols, such as ethanol, propanol or butanol; glycols as well as their ethers and esters, such as propylene glycol or dipropylene glycol ether, ketones such as cyclohexanone, isophorone or diacetone alcohol, strongly polar solvents such as N-methyl-2-pyrrolidone, dimethyl sulfoxide or water; vegetable oils as well as their esters, such as rapeseed oil, castor oil or soybean oil; and if appropriate also silicone oils.

Suitable surface-active compounds are non-ionic, cationic and/or anionic surfactants having good emulsifying, dispersing and wetting properties, depending on the nature of the active substance of the formula I to be formulated. Surfactants are also to be understood as meaning mixtures of surfactants.

Anionic surfactants which are suitable can be either so-called water-soluble soaps or water-soluble synthetic surface-active compounds.

Suitable soaps which may be mentioned are the alkali metal salts, alkaline earth metal salts or substituted or unsubstituted ammonium salts of higher fatty acids (C₁₀-C₂₂), such as the Na salts or K salts of oleic or stearic acid, or of natural mixtures of fatty acids which can be obtained, for example, from coconut oil or tallow oil. Mention must also be made of the fatty acid methyltaurates.

However, so-called synthetic surfactants are used more frequently, in particular fatty alcohol sulfonates, fatty alcohol sulfates, sulfonated benzimidazole derivatives or alkylarylsulfonates.

The fatty alcohol sulfonates or fatty alcohol sulfates are generally in the form of alkali metal salts, alkaline earth metal salts or substituted or unsubstituted ammonium salts, and have an alkyl radical having 8 to 22 C atoms, alkyl also including the alkyl moiety of acyl radicals, for example the Na or Ca salt of ligninsulfonic acid, of the dodecylsulfuric ester or of a fatty alcohol sulfate mixture prepared from natural fatty acids. This group also includes the salts of the sulfuric esters and sulfonic acids of fatty alcohol/ethylene oxide adducts. The sulfonated benzimidazole derivatives preferably contain 2 sulfonyl groups and one fatty acid radical having 8 to 22 C atoms. Examples of alkylarylsulfonates are the Na, Ca or triethanolamine salts of dodecylbenzenesulfonic acid, of dibutyl-naphthalenesulfonic acid or of a naphthalenesulfonic acid/formaldehyde condensation product.

Other suitable compounds are the corresponding phosphates, such as the salts of the phosphoric ester of a p-nonylphenol/(4-14)-ethylene oxide adduct, or phospholipids.

Suitable non-ionic surfactants are mainly polyglycol ether derivatives of aliphatic or cycloaliphatic alcohols, of saturated or unsaturated fatty acids and of alkylphenols, which can contain 3 to 30 glycol ether groups and 8 to 20 carbon atoms in the (aliphatic) hydrocarbon radical and 6 to 18 carbon atoms in the alkyl radical of the alkylphenols.

Other non-ionic surfactants which are suitable are the water-soluble polyethylene oxide adducts with polypropylene glycol, ethylenediaminopolypropylene glycol and alkylpolypropylene glycol which have 1 to 10 carbon atoms in the alkyl chain and which contain 20 to 250 ethylene glycol ether groups and 10 to 100 propylene glycol ether groups. The abovementioned compounds customarily contain 1 to 5 ethylene glycol units per propylene glycol unit.

Examples of non-ionic surfactants which may be mentioned are nonylphenolpolyethoxyethanols, castor oil polyglycol ethers, polypropylene/polyethylene oxide adducts, tributylphenoxypolyethoxyethanol, polyethylene glycol and octylphenoxypolyethoxyethanol.

Other suitable substances are fatty acid esters of polyoxyethylenesorbitan, such as polyoxyethylenesorbitan trioleate.

The cationic surfactants are mainly quaternary ammonium salts, which contain at least one alkyl radical having 8 to 22 C atoms as N-substituents and which have lower halogenated or free alkyl, benzyl or lower hydroxyalkyl radicals as further substituents. The salts are preferably in the form of halides, methylsulfates or ethylsulfates, for example stearyltrimethylammonium chloride or benzyldi(2-chloroethyl)ethylammonium bromide.

The surfactants customary in formulation technology are described, inter alia, in the following publications: "McCutcheon's Detergents and Emulsifiers Annual", Mc Publishing Corp., Glen Rock, New Jersey, 1988; M. and J. Ash. "Encyclopedia of Surfactants", Vol. I-III, Chemical Publishing Co., New York, 1980-1981. Dr. Helmut Stache, "Tensid-Taschenbuch [Surfactant Guide]", Carl Hanser Verlag, Munich, Vienna, 1981;

As a rule, the pesticidal preparations contain 0.1 to 99 %, in particular 0.1 to 95 %, of the active substance of the formula I, 1 to 99 % of a solid or liquid additive and 0 to 25 %, in particular 0.1 to 25 %, of a surfactant.

While concentrated compositions are more preferred as commercial goods, the user generally uses dilute compositions.

The compositions can also comprise further additives such as stabilisers, for example epoxidised or unepoxidised vegetable oils (epoxidised coconut oil, rapeseed oil or soybean oil), defoamers, for example silicone oil, preservatives, viscosity regulators, binders, tackifiers, as well as fertilisers or other active substances for achieving specific effects.

In particular, preferred formulations have the following composition: (% = per cent by weight)

Emulsifiable concentrates:

Active ingredient:	1 to 90 %, preferably 5 to 20 %
Surface-active agent:	1 to 30 %, preferably 10 to 20 %
Liquid carrier:	50 to 94 %, preferably 70 to 85 %

Suspension concentrates:

Active ingredient:	5 to 75 %, preferably 10 to 50 %
Water:	94 to 24 %, preferably 88 to 30 %
Surface-active agent:	1 to 40 %, preferably 2 to 30 %

As a rule, the active substances of the formula I are successfully employed at application rates from 0.001 to 10 kg/ha, in particular 0.005 to 2 kg/ha. The dosage rate which is required for the desired action can be determined by tests. It depends on the nature of the action, the development stage of the crop plant and the weed, as well as on the application (location, time, method) and, due to these parameters, can vary within wide limits.

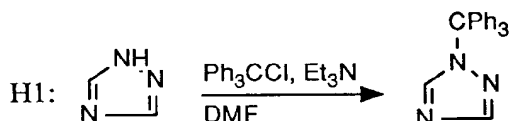
Controlled release of active substance

The dissolved active substance is applied to mineral granule carriers or polymerised granules (urea/formaldehyde) and allowed to dry. If desired, a coating can be applied (coated granules), which permits slow release of the active substance over a certain period.

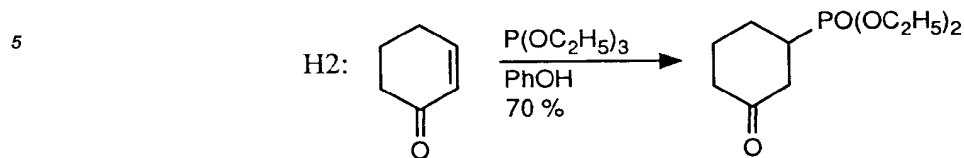
The following examples are intended to illustrate the invention in greater detail.

A. Preparation of compounds of formula I

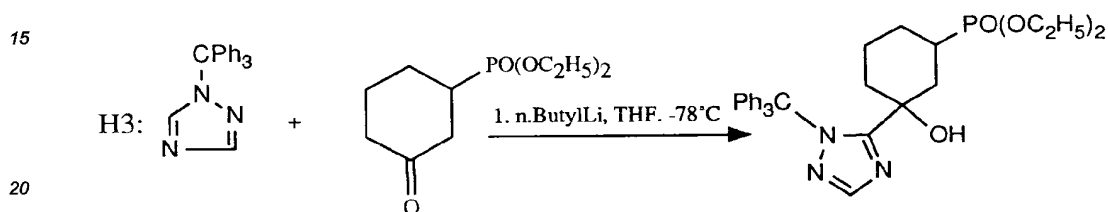
The preparation follows the following scheme



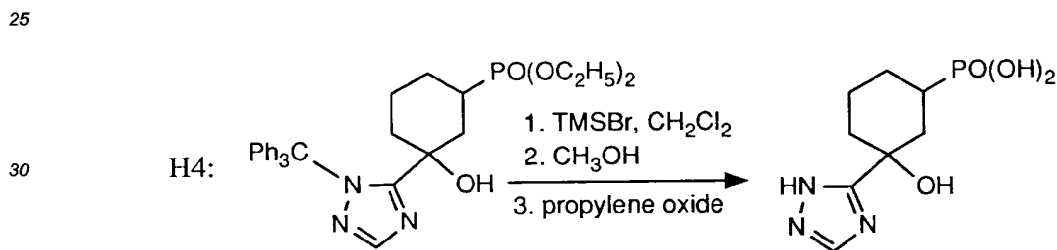
(Ph₃CCl = triphenylmethylchloride; Et₃N = triethylamine; DMF = dimethylformamide)



(P(OC₂H₅)₃ = triethylphosphite; PhOH = phenol)



(THF = tetrahydrofuran)

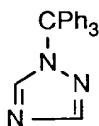


35 (TMSBr = trimethylsilylbromide)

Example H1:

40 To a mixture of 1H-1,2,4-triazole (75 g, 1.09 mol) and triphenylmethylchloride (302.7 g, 1.09 mol) in 1200 mL of dimethylformamide was added triethylamine (182 mL, 1.30 mol) dropwise with cooling in an ice bath. After completion of the addition, the mixture was allowed to warm to room temperature and stirred overnight. To the mixture, 1.5 L of water was added in 1.5 h. The precipitates were collected on a glass filter, washed with water (5 x 250 mL) and with ether (5 x 250 mL), and dried in vacuo to give 342 g (quant) of the compound of the formula

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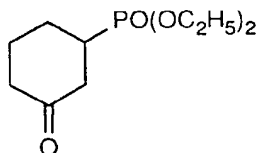
as slightly yellowish solid.

¹H NMR (90 MHz, CDCl₃) δ 8.07 (s, 1), 8.03 (s, 1), 6.95-7.49 (m, 15).

55 Example H2:

This compound was prepared according to the procedure described by Johnson. (Crooks, S.L.; Robinson, M. B.; Koerner, J. F.; Johnson, R. L. J. Med. Chem. 1986, 29, 1988-1995).

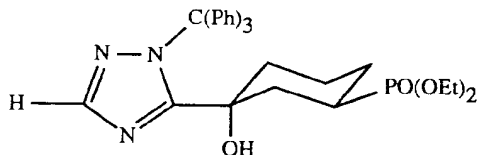
To a solution of 2-cyclohexen-1-one (25 mL, 0.26 mol) in 64.6 g of warm phenol (ca. 50°C) was added triethyl phosphite (56.8 mL, 0.32 mol) over 10 min via syringe. The temperature was maintained at 100°C for 24 h with an oil bath. Most of the remaining phenol was removed under reduced pressure (8 mmHg) at 50°C. Distillation at 133-139°C (0.3 mmHg) gave 42.6 g (70 % yield) of the compound of the formula



^1H NMR (90 MHz, CDCl_3) δ 3.95-4.27 (quintet, 4, $J = 7.3$), 1.45-2.49 (m, 9), 1.24-1.40 (t, 6, $J = 7.0$).

Example H3:

A clear solution of the compound obtained in Example H1 (10 g, 32 mmol) in 150 mL of warm tetrahydrofuran was cooled to -78°C. *n*-Butyllithium (38.4 mmol, in 1.5 M hexane) was added dropwise in 10 minutes and was stirred for 50 minutes at -78°C. *n*-Butyllithium has to be added before precipitation of the compound obtained in Example H1 starts. To the resulting reddish (sometimes yellow) solution was added the compound obtained in Example H2 (9.03 g, 38.4 mmol) and stirred for 1 h. The reaction was quenched with 50 mL of saturated aqueous ammonium chloride and was allowed to warm to room temperature. The mixture was diluted with 100 mL of water, extracted with chloroform, dried over MgSO_4 , and concentrated. Column chromatography on silica gel (400 g) with ethyl acetate then ethyl acetate/ethanol (20:1) gave 9.85 g (57 % yield) of the compound of the formula

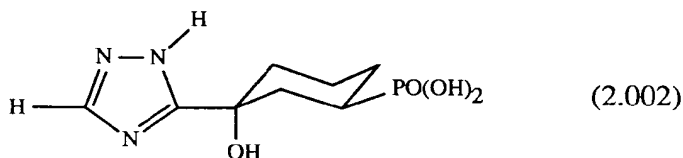


as a colorless solid.

^1H NMR (90 MHz, CDCl_3) δ 7.85 (s, 1), 7.10-7.31 (m, 15), 3.85-4.17 (quintet, 4, $J = 7.4$), 0.80-2.30 (m, 9), 1.20-1.36 (t, 6, $J = 7.2$).

Example H4:

To a solution of the compound obtained according to Example H3 (6.0 g 11.0 mmol) in 150 mL of CH_2Cl_2 was added trimethylsilyl bromide (7.27 mL, 55.0 mmol) in one portion and the mixture was stirred overnight at room temperature. After addition of methanol (75 mL) the mixture was stirred for 1 h at room temperature. Propylene oxide (15 mL) was added and the resulting mixture was stirred for another 1 h. Slow addition of 600 mL of ether caused precipitation of the desired compound. The precipitates were collected on a glass filter under a stream of nitrogen, washed 5 times with 50 mL of ether, and dried in vacuo to give 2.62 g (96 % yield) of trans-3-hydroxy-3-(1,2,4-triazole-3-yl)-cyclohexanephosphonic acid (compound no. 2.002) of the formula



mp 166°C decomp.

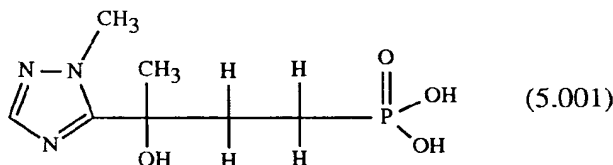
^1H NMR (90 MHz, D_2O) δ 8.80 (s, 1H), 1.1-2.5 (m, 9H).

Example H5:

a) To a solution of 1-methyl-1,2,4-triazole (3.0 g, 36.1 mmol) in tetrahydrofuran (60 ml) was added n-buthyllithium (43.3 mmol, 1.2 eq) at -78°C under nitrogen. The mixture was stirred for 1 hour, then diethyl 3-oxo-butylphosphonate (8.3 g, 39.7 mmol, 1.1 eq) was added. The mixture was stirred for 2 hours and quenched with aq. NH₄Cl (ca. 15 ml). The mixture was warmed to room temperature and extracted with CH₂Cl₂ (5 x 100 ml). The extract was dried over MgSO₄, concentrated in vacuo, and purified by a silica gel column chromatography (200 g, AcOEt-EtOH) to give (2.99g, 28 % yield) of diethyl 3-hydroxy-3-methyl-3-(1-methyl-1,2,4-triazol-5-yl)propyl-phosphonate.

¹H NMR (90 MHz, CDCl₃) δ 7.75 (s, 1H), 4.13 (s, 3H), 4.29-3.90 (m, 4H), 2.80-1.80 (m, 5H), 1.63 (s, 3H), 1.37 (t, 3H, J = 7.0 Hz), 1.33 (t, 3H, J = 7.0 Hz).

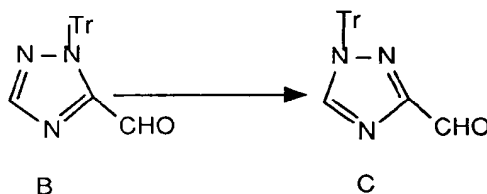
b) To a solution of diethyl 3-hydroxy-3-methyl-3-(1-methyl-1,2,4-triazol-5-yl)propyl-phosphonate (1.2 g, 4.12 mmol) in CH₂Cl₂ (24 ml) was added TMSBr (2.72 ml, 20.6 mmol, 5 eq) at room temperature under nitrogen. The reaction mixture was stirred for 16 hours. Then methanol (12 ml) was added to the mixture. After stirring for 2 hours, addition of propylene oxide (2.4 ml) and dilution with diethylether gave colourless precipitates which were collected on a glass filter under nitrogen, washed with diethylether, and dried in vacuo to give pure 3-hydroxy-3-methyl-3-(1-methyl-1,2,4-triazol-5-yl)propyl-phosphonic acid, compound no 5.001 (0.63 g, 65 % yield).



¹H NMR (90 MHz, D₂O) δ 8.31 (s, 1H), 4.16 (s, 3H), 2.37-1.48 (m, 4H), 1.72 (s, 3H), melting point 188-191 °C.

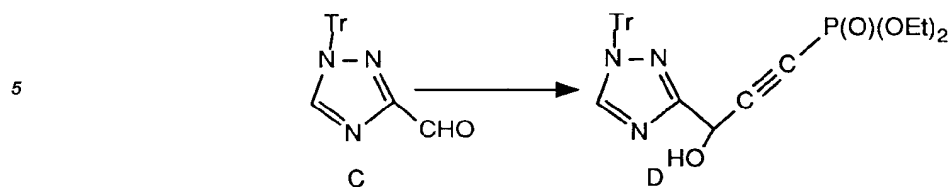
1-methyl-1,2,4-triazole was prepared according to the procedure by Dallacher and Minn, Chemiker-Zeitung 1986, **110**, 101-108.

In the following examples the substituent "Tr" is triphenylmethyl.

Example H6: Preparation of compound 1.012:

To a solution of Triazolecarbaldehyde B (73.7 g, 0.217 mol) in 1 l of CH₂Cl₂ was added 4N HCl in dioxane (59.7 mL, 0.239 mol) at room temperature and the mixture was stirred for 30 min. Tritylchloride (6.05 g, 0.0217 mol) and triethylamine (54.4 ml, 0.326 mol) were then added to this mixture at 0°C and stirred at room temperature for 1 h. The reaction was quenched with water and extracted with CH₂Cl₂. Combined organic layers were dried over MgSO₄, concentrated in vacuo, and triturated with ether to give triazolecarbaldehyde C (69.0 g, 94 %) as a colorless powder.

¹H NMR (90 MHz, CDCl₃) δ 10.04 (s, 1H), 8.13 (s, 1H), 7.47-6.98 (m, 15H).

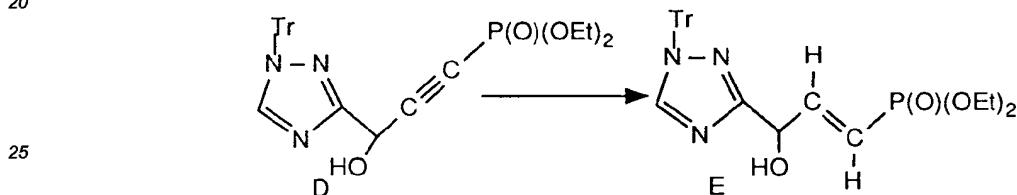


10

To a stirred solution of diethyl 2-(trimethylsilyl)ethynylphosphonate (0.234 g, 1.0 mmol) and triazolecarbaldehyde C (0.341 g, 1.0 mmol) in 5 ml of THF was added cesium fluoride (0.055 g, 0.36 mmol) at 0°C and the mixture was stirred for 3 h at the same temperature. The reaction was quenched with aq. NH₄Cl, extracted with CH₂Cl₂, dried over MgSO₄, and concentrated in vacuo. The resulting crude material was purified by silica gel chromatography (ethyl acetate:CH₂Cl₂ = 9:1) to give D (0.233 g, 46 %) as colorless solid: m.p. 155-157°C

15 ¹H NMR (90 MHz, CDCl₃) δ 7.98 (s, 1H), 7.48-6.95 (m, 15H), 5.69 (dd, 1H, J = 8.3 Hz, 3.8 Hz), 4.49 (bd, 1H, J = 8.3 Hz), 4.08 (quintet, 4H, J = 7.3 Hz), 1.27 (t, 6H, J = 7.0 Hz).

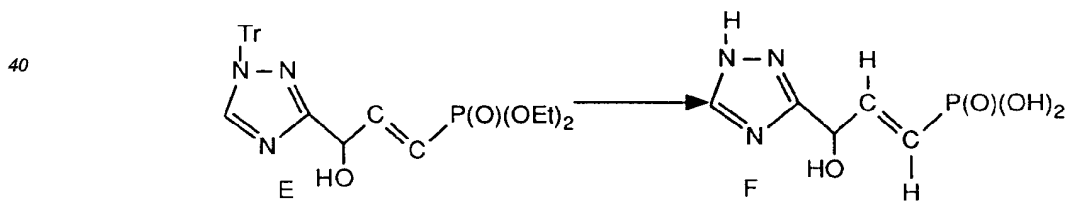
20



A solution of RedAl (0.29 ml, 3.4M in toluene, 1.0 mmol) in THF (3 ml) was added dropwise to a stirred solution of D (0.502 g, 1.0 mmol) in THF (5 ml) at -78°C. After stirring for 30 min at -78°C, the mixture was warmed to room temperature and stirred further for 10 min. The reaction was quenched by addition of aq. NH₄Cl and diluted with CHCl₃. The mixture was stirred for 24 h at room temperature and extracted with CHCl₃, dried over MgSO₄, and purified by silica gel chromatography (ethyl acetate:ethanol = 1:0 - 9:1) to give allyl alcohol E (0.165 g, 33 %) as a colorless solid: m.p. 118-122°C.

30

35 ¹H NMR (90 MHz, CDCl₃) δ 7.94 (s, 1H), 7.45-6.77 (m, 16H), 6.10 (ddd, 1H, J = 20.0 Hz, 16.9 Hz, 1.8 Hz), 5.63-5.39 (bs, 1H), 4.05 (m, 4H), 1.30 (t, 6H, J = 7.0 Hz).



45

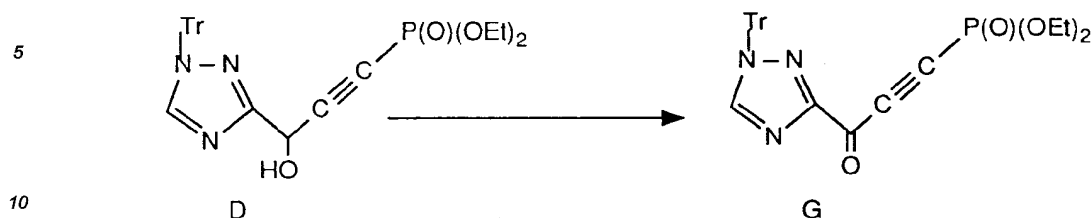
To a solution of allyl alcohol E (0.374 g, 0.74 mmol) in CH₂Cl₂ (4 ml) was added TMSBr (0.4 ml, 3.0 mmol) at room temperature. After the mixture was stirred overnight at room temperature, methanol (0.4 ml) was added and the mixture was stirred for additional 1 h. Propylene oxide (0.4 ml) was added and the resulting suspension was stirred for 2 h at room temperature. Ether was added to complete precipitation and the precipitates were collected and washed with ether to give pure F (Compound 1.012, 0.152 g, quant.) as a colorless solid.

50

¹H NMR (90 MHz, D₂O) δ 8.92 (s, 1H), 5.70 (m, 1H), 6.93-6.05 (m, 2H).

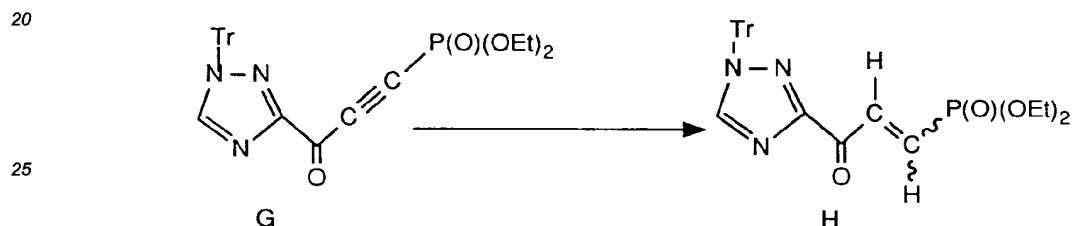
55

Example H7: Preparation of compound 4.001:



To a well stirred solution of D (0.850 g, 1.7 mmol) in CH_2Cl_2 (15 ml), manganese oxide (1.14 g, 13.1 mmol) was added at room temperature. After vigorous stirring for 2 h, additional manganese oxide (0.50 g, 5.8 mmol) was added at room temperature and the mixture was stirred further for 1 h. The reaction mixture was filtered through a silica gel column with CH_2Cl_2 and ethyl acetate to give pure G (0.675 g, 79 %) as a colorless solid: m.p. 95-101°C.

^1H NMR (90 MHz, CDCl_3) δ 8.09 (s, 1H), 7.47-6.98 (m, 15H), 4.13 (m, 4H), 1.26 (t, 6H, $J = 7.0$ Hz).



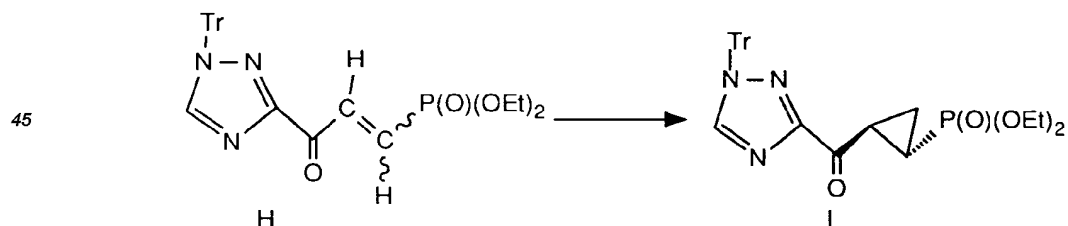
To a solution of G (3.0 g, 6.0 mmol) in methanol (30 ml) were added Pd on CaCO_3 (0.50 g) and quinoline (12 drops). The mixture was stirred under hydrogen atmosphere at room temperature for 7 h. The catalyst was filtered and washed with methanol and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane:ethyl acetate = 2:3 - 0:1) to give cis-H (0.60 g, 20 %) and trans-H (0.83 g, 28 %) in the order of elution.

cis-H: m.p. 89-92°C

^1H NMR (90 MHz, CDCl_3) δ 8.06 (s, 1H), 7.92-7.05 (m, 16H), 6.28 (dd, 1H, $J = 13.8$ Hz), 4.20 (m, 4H), 1.28 (t, 6H, $J = 7.0$ Hz).

trans-H: m.p. 105-110°C

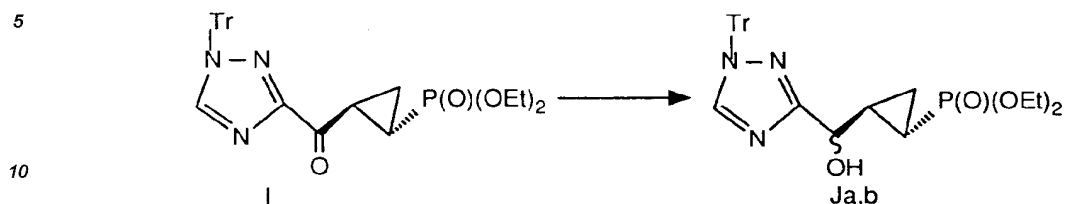
^1H NMR (90 MHz, CDCl_3) δ 8.11 (s, 1H), 8.08-6.88 (m, 17H), 4.20 (quintet, 4H, $J = 7.3$ Hz), 1.30 (t, 6H, $J = 7.0$ Hz).



To a stirred mixture of sodium hydride (0.025 g, 60 % in oil, 0.63 mmol) and trimethyloxosulfonium iodide (0.145 g, 0.65 mmol) was added DMSO (1 ml) slowly at room temperature and the mixture was stirred for 20 min at the same temperature. The resulting mixture of dimethyloxosulfonium methylide was then added to a solution of cis-H (0.300 g, 0.6 mmol) in DMSO (1 ml) at room temperature. After stirring for 40 min, the reaction was quenched with aq. NH_4Cl . The mixture was extracted with ethyl acetate, dried over MgSO_4 , and purified by silica gel chromatography (hexane:ethyl acetate: CH_2Cl_2 = 1:8:1) to give pure I (0.040 g, 13 %) as a colorless solid: m.p.: 135-138°C.

I was also obtained from trans-H in a 15 % yield by the same method as above.

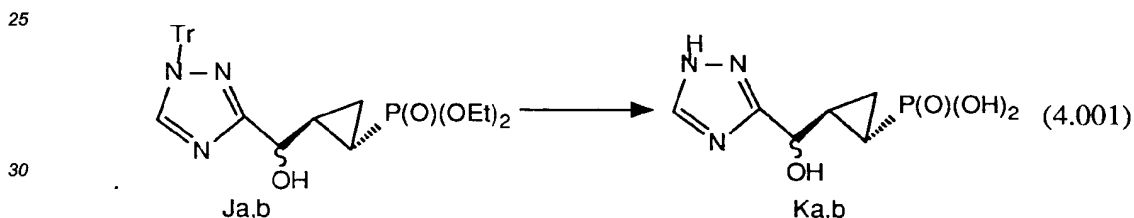
¹H NMR (90 MHz, CDCl₃) δ 8.08 (s, 1H), 7.46-6.95 (m, 15H), 4.27-3.83 (m, 4H), 3.77-3.28 (m, 1H), 1.95-1.08 (m, 9H).



15 Sodium borohydride (0.005 g, 0.13 mmol) was added to a solution of I (0.130 g, 0.25 mmol) in ethanol (2 ml) at room temperature and the mixture was stirred for 2 h. The reaction was quenched with brine and the mixture was extracted with ethyl acetate, dried over MgSO₄ and purified by medium pressure liquid chromatography on silica gel (ethyl acetate:ethanol = 39:1 - 19:1) to give Ja (0.046 g, 36 %) and Jb (0.043 g, 33 %) in the order elution.

20 Ja: ¹H NMR (90 MHz, CDCl₃) δ 7.92 (s, 1H), 7.42-7.05 (m, 15H), 4.58 (d, 1H, J = 6.3 Hz), 4.24-3.88 (m, 4H), 3.21 (br. 1H), 2.30-0.90 (m, 10H).

Jb: ¹H NMR (90 MHz, CDCl₃) δ 7.92 (s, 1H), 7.40-7.04 (m, 15H), 4.80 (br, 1H), 4.26-3.85 (m, 4H), 3.25 (br, 1H), 2.29-0.89 (m, 10H).



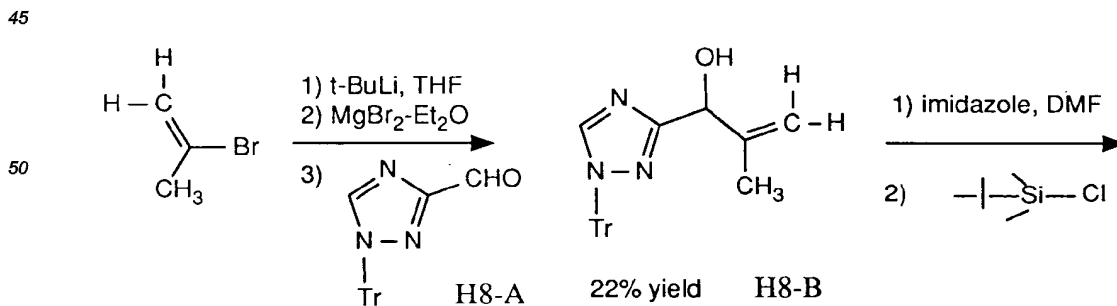
35 TMSBr (0.05 ml, 0.35 mmol) was added to a solution of Ja (0.046 g, 0.09 mmol, one isomer) in CH₂Cl₂ (0.5 ml) at room temperature and the mixture was stirred for 4 h. Additional TMSBr (0.02 ml, 0.15 mmol) was added and the mixture was stirred further for 1.5 h at room temperature and ether was added to complete precipitation. The precipitates were collected and washed with ether to give pure Ka (0.02 g, quant.) as a colorless solid.

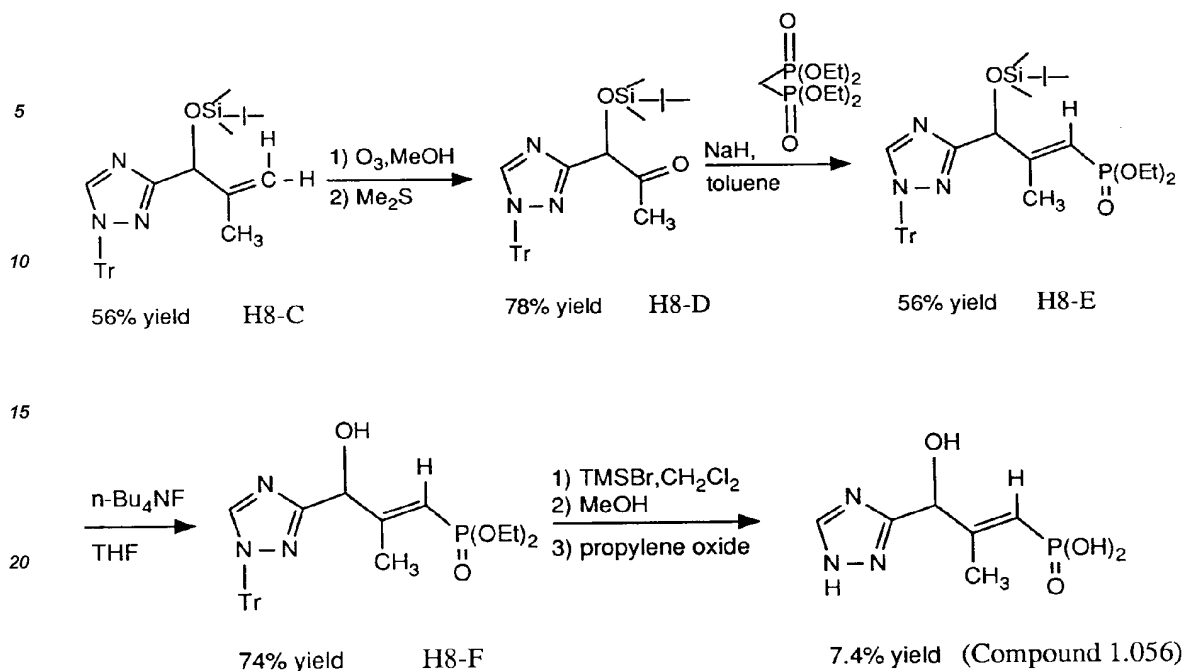
40 Ka: ¹H NMR (90 MHz, D₂O) δ 8.85 (s, 1H), 4.65 (d, 1H, J = 8.9 Hz), 2.30-0.95 (m, 4H).

Compound Jb was similarly deprotected to give a quantitative yield of Kb as a colorless solid.

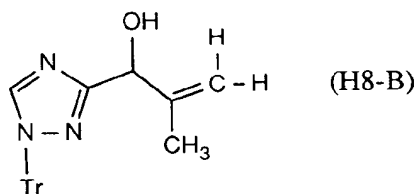
Kb: ¹H NMR (90 MHz, D₂O) δ 8.87 (s, 1H), 4.61 (d, 1H, J = 8.1 Hz), 1.98-0.90 (m, 4H).

Example H8: Preparation of compound 1.056





a) Preparation of compound H8-B:

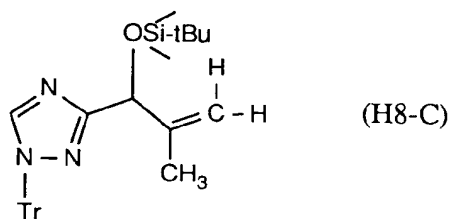


To a solution of 2-bromopropene (7.32 g, 60.5 mmol) in 450 ml of THF was added t-BuLi (74.7 ml, 1.7 m in pentane, 127.1 mmol) under nitrogen at -78°C. After 1 h, $\text{MgBr}_2 \cdot \text{Et}_2\text{O}$ (17.19 g, 66.6 mmol) was added to the mixture in one portion, then the mixture was allowed to warm to 0°C and stirred for 1 h. Aldehyde H8-A (24.6 g, 72.6 mmol) was added to the mixture and stirred at 0°C for 1.5 h. The reaction was quenched by addition of aq. NH_4Cl (40 ml), diluted with water, and extracted with CH_2Cl_2 (5 x 300 ml). The combined organic layers were dried over MgSO_4 , concentrated, and purified by silica gel chromatography ($\text{AcOEt}:\text{CH}_2\text{Cl}_2=1:5$) to give 5.08 g (22 % yield) of YK-79 as a colorless solid.

mp 111-112°C;

^1H NMR (90 MHz, CDCl_3) δ 7.90 (s, 1), 7.40-7.05 (m, 15), 5.32-5.15 (m, 2), 5.01-4.94 (m, 1), 2.98 (d, 1, $J=6.8$), 1.65 (d, 3, $J=3.3$).

b) Preparation of compound H8-C:



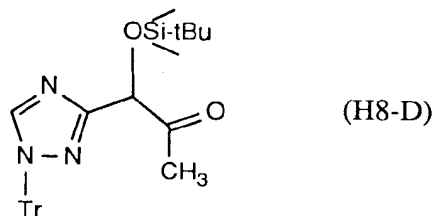
To a solution of compound H8-B (7.30 g, 19.1 mmol) in 100 ml of DMF was added imidazole (1.95 g, 28.7

mmol) at room temperature under nitrogen. The mixture was cooled to 0°C and t-butyldimethylsilyl chloride (3.17 g, 21.05 mmol) was added. After 30 min, the mixture was allowed to warm to room temperature and stirred for 18 h. Ice water was added to the mixture and extracted with AcOEt (4x100 ml). The combined organic layers were washed with water (6x100 ml), dried over MgSO₄, and concentrated. The residue was purified by silica gel chromatography (AcOEt:hexane = 1:4 to 1:1) to give 5.30 g (56 % yield) of compound H8-C as a colorless solid.

mp 81-83°C;

¹HNMR (90 MHz, CDCl₃) δ 7.77 (s,1), 7.25-7.05 (m,15), 5.16 (m,2) 4.84 (m,1), 1.56 (s,3), 0.75 (s,9), -0.07 (s,3), -0.17 (s,3).

c) Preparation of compound H8-D:

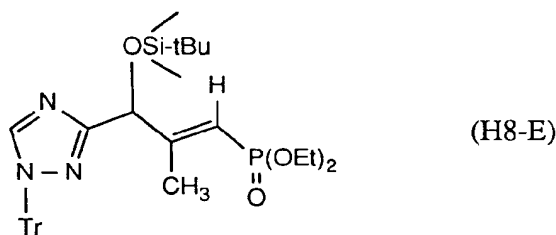


To a solution of compound H8-C (1.0 g, 2.0 mmol) in methanol (10 ml) was passed ozonized oxygen (ca. 5 mmol) at -78°C. After the reaction mixture was flushed with nitrogen and dimethyl sulfide (1.48 ml, 20.2 mmol) was added at -78°C, the mixture was allowed to warm to room temperature, and stirred for 5 h. Concentration and purification by silica gel chromatography gave 780 mg (78 % yield) of compound H8-D.

mp 80-83°C;

¹HNMR (90 MHz, CDCl₃) δ 7.81 (s,1), 7.25-6.99 (m,15), 5.11 (s,1) 2.19 (s,3), 0.76 (s,9), -0.04 (s,3).

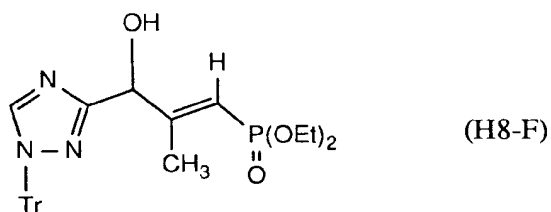
d) Preparation of compound H8-E:



To a suspension of NaH (60 % dispersion in mineral oil, 118 mg, 2.96 mmol) in 10 ml of toluene was added a solution of tetraethyl methylenediphosphonate (854 mg, 2.96 mmol) in 8 ml of toluene under nitrogen at room temperature. When a clear solution was formed, compound H8-D (1.34 g, 2.69 mmol) in 10 ml of toluene was added and stirred for 1 h at room temperature. A mixture of 45 ml of water and 90 ml of CHCl₃ was added and the aqueous layer was extracted with CHCl₃. The combined organic layers were dried over MgSO₄, concentrated, and purified by silica gel chromatography (AcOEt:hexane = 1:1 to 10:1) to give 950 mg (56 % yield) of the title compound as an oil.

¹HNMR (90 MHz, CDCl₃) δ 7.91 (s,1), 7.41-7.06 (m,15), 6.10 (broad d,1, J=18.0), 5.27 (m,1) 4.20-3.84 (m,4), 1.95 (d,3, J=3.3), 1.28 (t,3, J=7.0), 1.26 (t,3, J=7.0), 0.87 (s,9), 0.07 (s,3), -0.05 (s,3).

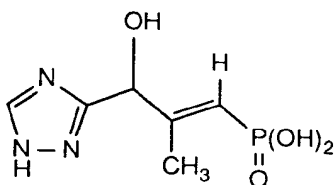
e) Preparation of compound H8-F:



To a solution of compound H8-E (840 mg) in 20 ml of THF was added $n\text{-Bu}_4\text{NF}$ (0.42 mmol, 1.0 m in THF) under nitrogen at room temperature. After 30 min, the reaction mixture was diluted with 200 ml of water and extracted with CH_2Cl_2 (4x50 ml). The combined organic layers were dried over MgSO_4 , concentrated, and purified by silica gel chromatography (AcOEt only) to give 510 mg (74 % yield) of compound H8-F as a white solid.

mp 150-152°C;
 ^1H NMR (90 MHz, CDCl_3) δ 7.93 (s,1), 7.42-7.04 (m,15), 5.99 (broad d,1, $J=17.4$), 5.27 (m,1), 4.24-3.86 (m,4), 2.00 (dd,3, $J=0.7,3.3$), 1.26 (t,3, $J=7.0$), 1.24 (t,3, $J=7.0$).

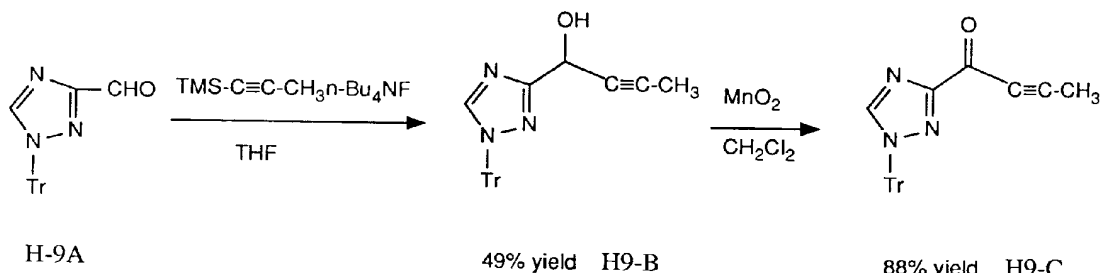
f) Preparation of compound 1.056:

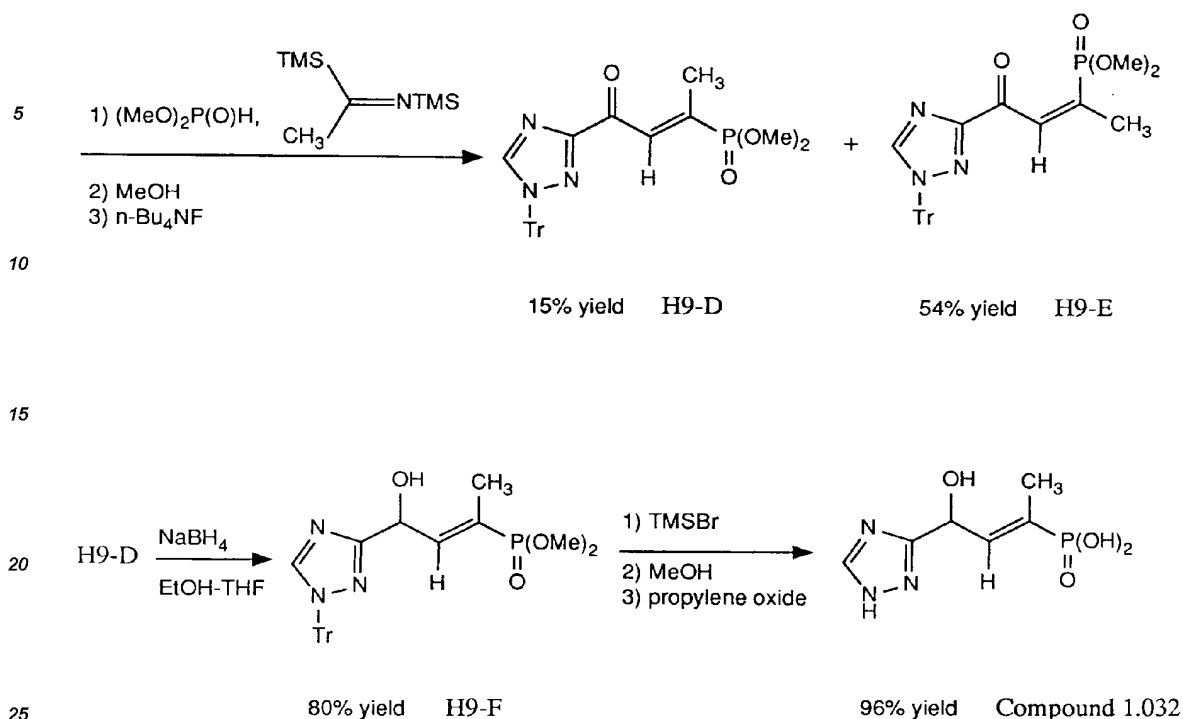


To a solution of compound H8-F (318 mg, 0.61 mmol) in 12 ml of CH_2Cl_2 was added trimethylsilyl bromide (0.41 ml, 3.07 mmol) under nitrogen at room temperature. After stirring for 16 h, methanol (6 ml) was added to the mixture and stirred for 2 h, and then propylene oxide (1.2 ml) was added. Ether was added slowly until precipitation was completed. Precipitates were collected and further purified with medium pressure liquid chromatography using a reverse phase column to afford 10 mg (7.4 % yield) of the title compound.

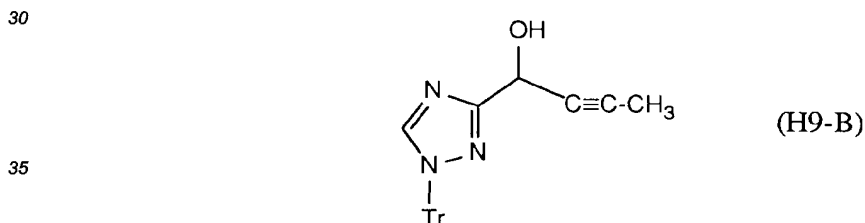
mp 92-105°C;

^1H NMR (90 MHz, D_2O) δ 8.27 (broad s,1), 6.10 broad d,1, $J=16.7$), 5.50 (broad s,1), 1.92 (d,3, $J=2.9$).

Example H9: Preparation of compound 1.032



a) Preparation of compound H9-B:

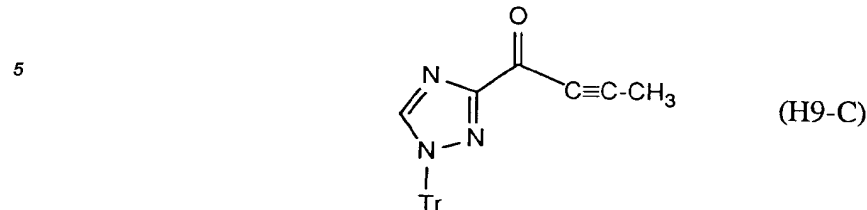


To a solution of aldehyde H9-A (10.0 g, 29.5 mmol) in 200 ml of THF were added 1-(trimethylsilyl)-1-propyne (5.01 ml, 33.9 mmol) and tetrabutylammonium fluoride (0.5 mmol, 1.0 m in THF) under nitrogen at 0°C. After stirring for 1.5 h at 0°C and for 21 h at room temperature, the mixture was cooled to 0°C and an additional tetrabutylammonium fluoride (8.5 mmol, 1.0 m in THF) was added. After 2 h, an additional 1-(trimethylsilyl)-1-propyne (2.18 ml, 14.7 mmol) was added to the mixture at 0°C and the mixture was allowed to warm to room temperature and stirred for 30 min. The reaction mixture was diluted with 200 ml of water and extracted with AcOEt (3 x 100 ml). The combined organic layers were dried over MgSO_4 , concentrated, and purified by silica gel chromatography ($\text{AcOEt}:\text{hexane}:\text{CH}_2\text{Cl}_2 = 2:2:1$) to give 5.47 g (49 % yield) of compound H9-B as a colorless solid.

mp 190-194°C;

^1H NMR (90 MHz, CDCl_3) δ 7.93 (s,1), 7.42-7.06 (m,15), 5.48-5.65 (m,1), 3.25 (broad d,1, $J=7.7$), 1.87 (d,3, $J=2.4$).

b) Preparation of compound H9-C:

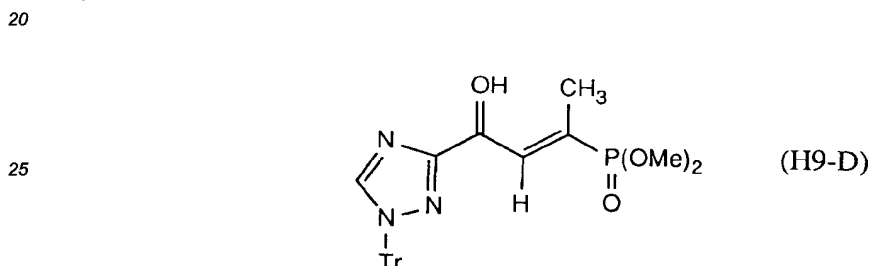


To a suspension of compound H9-B (3.50 g, 9.22 mmol) in 140 ml of CH₂Cl₂ was added MnO₂ (4.0 g, 46.1 mmol) in portions, and stirred for 70 min. After addition of Celite (8.0 g), the mixture was directly subjected to a silica gel column. Elution with a solvent mixture (AcOEt:hexane:CH₂Cl₂=2:2:1) afforded 3.06 g (88 % yield)

of compound H9-C as a colorless solid.

mp 151-154°C;
¹HNMR (90 MHz, CDCl₃) δ 8.02 (s,1), 7.40-7.10 (m,15), 2.12 (2,3).

c) Preparation of compound H9-D:

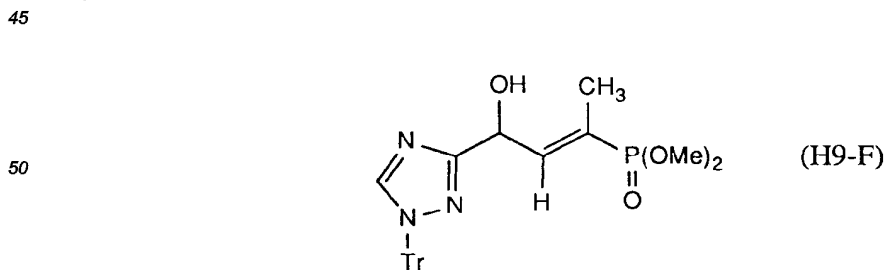


To a solution of compound H9-C (3.0 g, 7.95 mmol) in 45 ml of CH₂Cl₂ were added dimethyl phosphite (0.87 ml, 9.54 mmol) and N,O-bis(trimethylsilyl)acetamide (2.14 ml, 8.74 mmol) under nitrogen at room temperature. After stirring for 4 h at room temperature, and for 21 h under reflux, methanol (20 ml) and n-Bu₄NF (1.43 mmol, 1.0 M in THF) were added to the mixture at room temperature. After 1 h, the reaction was quenched by addition of water (100 ml) and extracted with CH₂Cl₂ (3 x 500 ml) and then with AcOEt (2 x 50 ml). The combined organic layers were dried over MgSO₄, concentrated, and purified by silica gel chromatography (AcOEt:hexane:CH₂Cl₂ = 2:1:1) to afford 580 mg (15 % yield) of the desired product as an oil, along with its stereo isomer H9-E (2.1 g, 54 % yield).

H9-D ¹HNMR (90 MHz, CDCl₃) δ 8.06 (s,1), 7.80 (broad d, 1, J=26.2.), 7.40-7.01 (m,15), 3.74 (d,6, J=11.0), 2.32 (dd, 3, J=16.9, 1.6).

H9-E mp 140-144°C; ¹HNMR (90 MHz, CDCl₃) δ 8.0 (s,1), 7.21 (broad d, 1, J=45.3.), 7.50-7.05 (m,15), 3.70 (d,6, J=11.0), 2.11 (dd, 3, J=13.4, 1.8).

d) Preparation of compound H9-F:



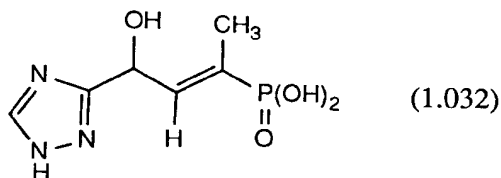
To a solution of compound H9-D (400 mg, 0.821 mmol) in 10 ml of a solvent mixture (ethanol:THF = 1:1) was added NaBH₄ (15.5 mg, 0.41 mmol) under nitrogen at room temperature. After 15 min, water (50 ml) and sat. aq NH₄Cl (1 ml) were added and the mixture was extracted with CH₂Cl₂ (2 x 30 ml) and with AcOEt (3 x

40 ml). The combined organic layers were dried over MgSO_4 , concentrated, and purified by silica gel chromatography (AcOEt only) to give 321 mg (80 % yield) of compound H9-F as a colorless solid.

mp 158-162°C;

^1H NMR (90 MHz, CDCl_3) δ 7.95 (s,1), 7.51-6.94 (m,15), 6.75 (ddd,1, $J=23.3$, 7.6, 1.4), 5.73-5.59 (m,1), 3.80 (dd,6, $J=11.0$, 5.5), 1.85 (dd,3, $J=15.0$, 1.5).

e) Preparation of compound 1.032:

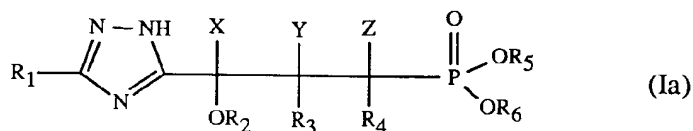


To a solution of compound H9-F (280 mg, 0.57 mmol) in 8 ml of CH_2Cl_2 was added trimethylsilyl bromide (0.38 ml, 2.86 mmol) under nitrogen at room temperature. After 15 h, methanol (4 ml) was added and stirred for 2 h. After addition of propylene oxide (0.8 ml), ether was added slowly at 0°C. Resulting precipitates were collected, washed with ether, and dried to give 120 mg (96 % yield) of the title compound as a white powder. mp 97-99°C decomp.;

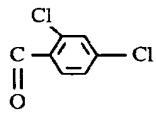
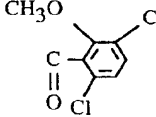
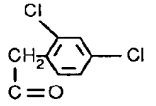

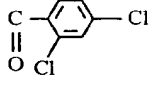




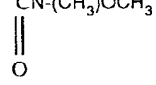

^1H NMR (90 MHz, D_2O) δ 8.90 (s,1), 6.56-6.21 (m,1), 5.90 (dd,1, $J=8.5$, 2.5), 1.95 (dd,3, $J=14.3$, 1.1).


Compounds of the formulae Ia, Ib, Ic, Id, Ii, Ij and Ik which are listed in the Tables 1 to 7 are prepared analogously to Examples H1 to H9.

Table 1: Compounds of the formula Ia:



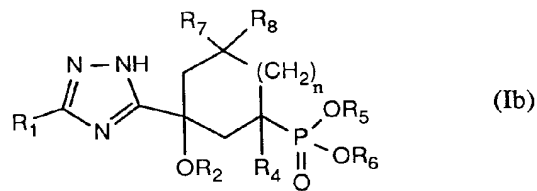
Comp. No.	R ₁	R ₂	X	Y	R ₃	R ₄	Z	R ₅	R ₆
1.001	H	H	C ₂ H ₅	H	H	H	C ₂ H ₅	H	H
1.002	H	H	CH ₃	H	H	CH ₃	CH ₃	H	H
1.003	H	H	CH ₃	CH ₃	CH ₃	H	H	H	H
1.004	H	H	CH(CH ₃) ₂	H	H	H	H	H	H
1.005	CH ₃	H	C ₂ H ₅	H	H	H	C ₂ H ₅	H	H
1.006	H	$\begin{array}{c} \text{CCH}_3 \\ \\ \text{O} \end{array}$	C ₂ H ₅	H	H	H	H	H	C ₂ H ₅
1.007	H	H	C ₂ H ₅	H	H	H	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅
1.008	H	H	CH ₃	H	H	H	H	H	H
1.009	H	H	C ₂ H ₅	H	H	H	H	H	H
1.010	H	H	(CH ₂) ₂ CH ₃	H	H	H	H	H	H
1.011	H	H	(CH ₂) ₃ CH ₃	H	H	H	H	H	H
1.012	H	H	H	H	bond		H	H	H
1.013	H	H	CH ₃	H	CH ₃	H	H	H	H
1.014	H	$\begin{array}{c} \text{CC}_2\text{H}_5 \\ \\ \text{O} \end{array}$	H	H	H	H	H	H	H
1.015	H	$\begin{array}{c} \text{CC}_3\text{H}_7\text{-i} \\ \\ \text{O} \end{array}$	H	H	H	H	H	H	H
1.016	H	$\begin{array}{c} \text{Cl} \\ \\ \text{C} - \text{C}_6\text{H}_4 \\ \quad \\ \text{O} \quad \text{Cl} \end{array}$	H	H	H	H	H	H	H

Comp. No.	R ₁	R ₂	X	Y	R ₃	R ₄	Z	R ₅	R ₆
1.017	H		H	H	H	H	H	H	H
1.018	H		H	H	H	H	H	H	H
1.019	H		H	H	H	H	H	H	H
1.020	H		CH ₃	H	H	H	H	H	H
1.021	H		CH ₃	H	H	H	H	H	H
1.022	H		H	H	H	H	H	H	H
1.023	H		H	H	H	H	H	H	H
1.024	H		H	H	H	H	H	H	H
1.025	H		H	H	H	H	H	H	H
1.026	H		H	H	H	H	H	H	H
1.027	H		CH ₃	H	H	H	H	H	H

	Comp. No.	R ₁	R ₂	X	Y	R ₃	R ₄	Z	R ₅	R ₆
5										
10	1.028	H	$\text{CN}(\text{C}_2\text{H}_5)_2$	H	H	H	H	H	H	H
			\parallel O							
	1.029	H	H	CH ₃	H	bond		H	H	H
	1.030	H	H	CH ₃	H	H	H	CH ₃	H	H
15	1.031	H	H	CH ₃	H	H	CH ₃	H	H	H
	1.032	H	H	H	H	bond		CH ₃	H	H
	1.033	H	CCH_3	H	H	bond		CH ₃	H	H
			\parallel O							
20	1.034	H	H	CH ₃	H	bond		CH ₃	H	H
	1.035	H	CCH_3	CH ₃	H	bond		CH ₃	H	H
			\parallel O							
25	1.036	H	H	H	H	bond		H	H	CH ₃
	1.037	H	CCH_3	H	H	bond		H	H	H
			\parallel O							
30	1.038	H	H	CH ₃	CH ₃	bond		H	H	H
	1.039	H	CCH_3	CH ₃	CH ₃	bond		H	H	H
			\parallel O							
35	1.040	H	H	H	H	bond		CH ₃	H	H
	1.041	H	CCH_3	H	H	bond		CH ₃	H	H
			\parallel O							
40	1.042	H	H	CH ₃	CH ₃	bond		CH ₃	H	H
	1.043	H	CCH_3	CH ₃	CH ₃	bond		CH ₃	H	H
			\parallel O							
45	1.044	H	H	CF ₃	H	H	H	H	H	H
	1.045	H	H		H	H	H	H	H	H
	1.046	H	$\text{CCH}_2\text{OOCCH}_3$	H	H	H	H	H	H	H
			\parallel O							
50										
55										

Comp. No.	R ₁	R ₂	X	Y	R ₃	R ₄	Z	R ₅	R ₆
1.047	H	$\text{CCH}_2\text{COOC}_2\text{H}_5$	H	H	H	H	H	H	H
		\parallel							
		O							
1.048	H	H CH ₂ OH	H	H	H	H	H	H	H
1.049	H	C(CH ₂) ₅ CH ₃	H	H	H	H	H	H	H
		\parallel							
		O							
1.050	H	COCH ₂ CH ₃	H	H	H	H	H	H	H
		\parallel							
		O							
1.051	CH ₃	H H	H	H	H	H	H	H	H
1.052	H	CCH ₃ CH ₃	H	H	H	H	H	H	H
		\parallel							
		O							
1.053	H	$\text{C} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{H}$	H	H	H	H	H	H	H
		O							
1.054	H	Ct-Butyl	H	H	H	H	H	H	H
		\parallel							
		O							
1.055	H	CSCH ₂ CH ₃	H	H	H	H	H	H	H
		\parallel							
		O							
1.056	H	H H	CH ₃	bond	H	H	H	H	H
1.057	CH ₃	H H	H	H	H	H	H	H	H

Table 2: Compounds of the formula Ib:






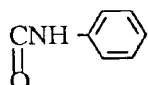
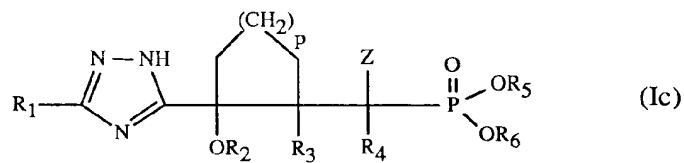
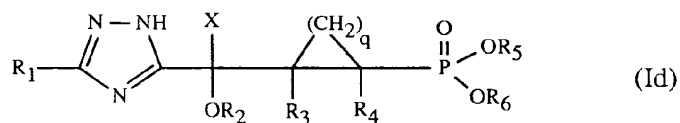
Comp. No.	Isom.	R ₁	R ₂	n	R ₄	R ₇	R ₈	R ₅	R ₆
2.001		H	H	1	H	H	H	C ₂ H ₅	C ₂ H ₅
2.002	trans	H	H	1	H	H	H	H	H
2.003		H	H	0	CH ₃	H	H	H	H
2.004		H	H	1	CH ₃	CH ₃	CH ₃	H	H
2.005		H	H	1	CH ₃	H	H	CH ₂ - 	CH ₂ - 
2.006		CH ₃	H	1	CH ₃	H	H	H	H
2.007		H		1	H	H	H	H	H
2.008		H		1	H	H	H	H	H
2.009	trans	H	H	1	CH ₃	H	H	H	H
2.010	cis	H	H	2	H	H	H	H	H

Table 3: Compounds of the formula Ic:



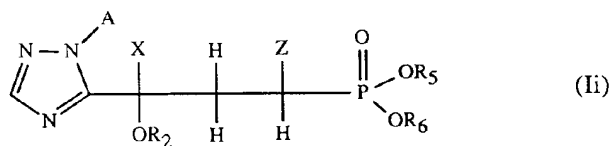
Compound No	R ₁	R ₂	p	R ₃	Z	R ₄	R ₅	R ₆
3.001	H	H	1	H	H	H	H	H
3.002	H	H	2	H	H	H	H	H

Table 4: Compounds of the formula Id:



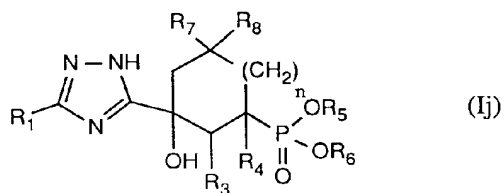
Compound No	R ₁	R ₂	X	q	R ₃	R ₄	R ₅	R ₆
4.001	H	H	H	1	H	H	H	H
4.002	H	H	CH ₃	2	H	H	H	H
4.003	H	H	CH ₃	3	H	H	H	H
4.004	H	H	H	4	H	H	H	H
4.005	H	H	CH ₃	4	H	H	H	H

Table 5: Compounds of the formula Ii:



Comp. No.	Isomer A	X	Z	R ₂	R ₅	R ₆
5.001		CH ₃	CH ₃	H	H	H
5.002	cis	CH ₃	-(CH ₂) ₃ -	-	H	H
5.003	trans	CH ₃	-(CH ₂) ₃ -	-	H	H
5.004		CH ₂ CH ₂ CH ₃	CH ₃	H	H	H
5.005	cis	CH ₂ CH ₃	-(CH ₂) ₃ -	-	H	H
5.006	trans	CH ₂ CH ₃	-(CH ₂) ₃ -	-	H	H
5.007		CH ₂ CH ₃	CH ₃	H	H	H
5.008	cis	CH ₃	-(CH ₂) ₂ -	-	H	H
5.009	trans	CH ₃	-(CH ₂) ₂ -	-	H	H
5.010		CH ₃	CH ₃	H	$\begin{array}{c} \text{CCH}_3 \\ \\ \text{O} \end{array}$	H
5.011	allyl	CH ₃	H	H	H	H
5.012	CH ₂ CH ₂ OH	CH ₃	H	H	H	H

Table 6: Compounds of the formula Ij:





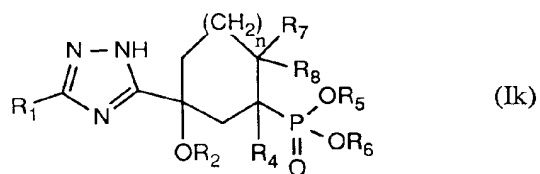
Comp. Isomer No.	R ₁	R ₃	n	R ₄	R ₇	R ₈	R ₅	R ₆
6.001 trans	H	CH ₃	1	H	H	H	H	H
6.002	H	H	1	CH ₃	H	H	H	H
6.003	H	H	0	CH ₃	H	H	H	H
6.004	H	H	1	CH ₃	CH ₃	CH ₃	H	H
6.005	H	H	1	CH ₃	H	H	CH ₂ - 	CH ₂ - 
6.006	CH ₃	H	1	CH ₃	H	H	H	H
6.007	H	C ₂ H ₅	1	H	H	H	H	H
6.008	H	n-C ₃ H ₇	1	H	H	H	H	H

Table 7: Compounds of the formula Ik:



Comp. Isom. No.	R ₁	R ₂	n	R ₄	R ₇	R ₈	R ₅	R ₆
7.001 cis	H	H	1	H	CH ₃	CH ₃	H	H
7.002 trans	H	H	1	H	CH ₃	CH ₃	H	H

Table 8: Physical data of the compounds of the formula I:

5	1.002	m.p. 175-176 °C (decomp.)
	1.009	m.p. 155-158 °C
	1.010	m.p. 87 °C (decomp.)
10	1.013	m.p. 80 °C (decomp.)
	1.014	m.p. 80-80 °C (decomp.)
	1.015	m.p. 98 °C (decomp.)
15	1.017	m.p. 127 °C (decomp.)
	1.019	m.p. 78 °C (decomp.)
	1.022	m.p. 96 °C (decomp.)
20	1.023	m.p. 103 °C (decomp.)
	1.024	m.p. 151 °C (decomp.)
	1.025	m.p. 96 °C (decomp.)
25	1.028	m.p. 85 °C (decomp.)
	1.030	m.p. 80 °C 3(S),2(R)-configuration
	1.031	m.p. 80 °C 3(S),2(S)-configuration
30	1.032	m.p. 97-99 °C (decomp.)
	1.045	m.p. 112 °C (decomp.)
	1.046	m.p. 99 °C (decomp.)
35	1.047	m.p. 90 °C (decomp.)
	1.049	m.p. 78 °C
	1.050	m.p. 88 °C (decomp.)
40	1.051	solid
	1.052	m.p. 135-140 °C
	1.053	m.p. 85 °C (decomp.)
45	1.054	m.p. 193-195 °C
	1.055	m.p. 98 °C (decomp.)
	1.056	m.p. 92-105 °C (decomp.)
50	2.002	m.p. 166 °C (decomp.)
	2.004	m.p. 195-198 °C
	2.007	m.p. 184-186 °C
55	2.009	m.p. 210-212 °C
	2.012	m.p. 197-198 °C (decomp.)
	5.001	m.p. 188-191 °C
	5.002	m.p. 120-125 °C

	5.003	m.p. 226-229°C
5	5.004	m.p. 146-148°C
	5.006	m.p. 213-218°C
	5.007	m.p. 152-155°C
	5.008	m.p. 170-174°C
10	5.009	m.p. 230-235°C
	5.011	m.p. 126-127.5 °C
	6.001	m.p. 201-203 °C (decomp.)
15	7.001	m.p. 125 °C (decomp.)
	7.002	m.p. 168 °C (decomp.)

20 Formulation examples of active substances of the formula I (% = percent by weight)

	1. <u>Emulsion concentrates</u>	a) b)	
	Active substance from Table 1-7	10 %	1 %
25	Ca dodecylbenzenesulfonate	3 %	3 %
	Octylphenol polyethylene glycol ether (4-5 mol of EO)	3 %	3 %
30	Castor oil polyethylene glycol ether (36 mol of EO)	4 %	4 %
	Cyclohexanone	30 %	10 %
	Xylene mixture	50 %	79 %

Emulsions of any desired concentration can be prepared from such concentrates by diluting them with water.

40	2. <u>Suspension concentrate</u>	a)	b)
	Active substance from Table 1-7	5 %	40 %
45	Ethylene glycol	10 %	10 %
	Nonylphenol polyethylene glycol ether (15 mol of EO)	1 %	6 %
50	Na ligninsulfonate	5 %	10 %
	Carboxymethylcellulose	1 %	1 %
	37 % aqueous formaldehyde solution	0.2 %	0.2 %
	Silicone oil in the form of a 75% aqueous emulsion	0.8 %	0.8 %
55	Water	77 %	32 %

The finely-ground active substance is mixed intimately with the additives. This gives a suspension concentrate, from which suspensions of any desired concentration can be prepared by diluting it with water.

3. Salt solution

Active substance from Table 1-7	5 %
Isopropylamine	1 %

Octylphenol polyethylene glycol ether (78 mol of EO)	3 %
Water	91%

The compounds of the formula I are employed as such or preferably as compositions together with the auxiliaries customary in formulation technology, and they are therefore processed in a known manner to give, for example, emulsion concentrates, directly sprayable or dilutable solutions, dilute emulsions, sprayable powders, soluble powders, dusts, granules, and also encapsulations, for example in polymeric substances. The application methods, such as spraying, atomising, dusting, scattering or pouring, as well as the type of compositions are selected to suit the intended aims and the prevailing circumstances.

Biological Examples

Example B1: Herbicidal action before emergence of the plants

The test plants are seeded out in plastic pots containing standard soil. Immediately after seeding, the pots are being sprayed with an aqueous suspension of the compound No. 2.002. The rate corresponds to 4000g a.i./ha. The treated pots are then placed in the greenhouse at temperatures of 18°C (night) and 24°C (day). Appr. 3 weeks after treatment, the emerged plants are evaluated in terms of herbicidal symptoms:

- 1: plants have not emerged or are totally withered
- 2-3: very pronounced action
- 4-6: medium action
- 7-8: weak action
- 9: no action (as untreated controls).

In this test, the compound 2.002 given in Table 2 shows very pronounced herbicidal action (rating "3") against the weed "Setaria".

Example B2: Post-emergence herbicidal action (contact herbicide)

The test plants are seeded out in plastic pots containing standard soil and raised in the greenhouse at 18°C (night) and 24°C (day). Appr. 10 to 20 days after seeding (depending of individual growth-rate), foliar treatment takes place with an aqueous suspension of compound No. 2.002. The rate corresponds to 4000g a.i./ha. Appr. 2 weeks after treatment, the emerged plants are evaluated in terms of herbicidal symptoms:

- 1: plants have not emerged or are totally withered
- 2-3: very pronounced action
- 4-6: medium action
- 7-8: weak action
- 9: no action (as untreated controls).

In this test, the compound 2.002 given in Table 2 shows very pronounced herbicidal action (rating "3") against the weed "Stellaria" and medium action (rating "4" against the weed "Sinapis".

Example B3: Post-emergence herbicidal action (contact herbicide)

The test plants are seeded out in plastic pots containing standard soil and raised in the greenhouse at 18°C (night) and 24°C (day). Appr. 10 to 20 days after seeding (depending of individual growth-rate), foliar treatment takes place with an aqueous suspension of compound No. 5.001. The rate corresponds to 2000g a.i./ha. Appr. 2 weeks after treatment, the emerged plants are evaluated in terms of herbicidal symptoms:

1: plants have not emerged or are totally withered

2-3: very pronounced action

4-6: medium action

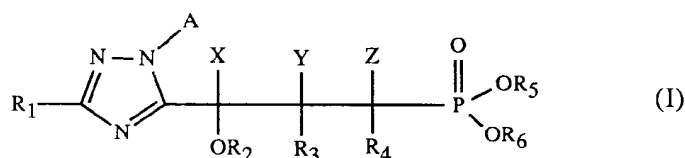
7-8: weak action

5 9: no action (as untreated controls).

In this test, the compound 5.001 given in Table 5 shows very pronounced herbicidal action (rating "3") against the weeds "Stellaria" and "Setaria".

10 Claims

1. A triazole of the formula I



in which

A is hydrogen, C₁-C₄-alkyl, C₁-C₄-alkenyl, triphenylmethyl, benzyl, a group

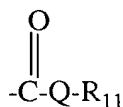


or C₁-C₄-alkyl substituted by hydroxy or C₁-C₄-alkoxy;

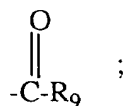
t is 4 or 5;

R₁ is hydrogen, fluorine or C₁-C₄-alkyl;

R₂ is hydrogen, a group



40 or a group



R₃ is hydrogen or C₁-C₄-alkyl;

R₄ is hydrogen or C₁-C₄-alkyl, or R₃ and R₄ together represent a chemical bond;

50 R₅ is hydrogen, C₁-C₄-alkyl, benzyl or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation;

R₆ is hydrogen, C₁-C₄-alkyl, benzyl or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation;

55 X is hydrogen, C₁-C₄-alkyl, C₃-C₆-cycloalkyl, C₁-C₄-haloalkyl, C₁-C₄-alkyl substituted by hydroxy or C₁-C₄-alkyl substituted by -OR₁₄;

Y is hydrogen or C₁-C₄-alkyl or together with X a -CH₂-(CH₂)_p-CH₂- group or together with Z a C₁-C₄-alkylene bridge which is substituted by R₇ and R₈;

Z is hydrogen or C₁-C₄-alkyl or together with X a C₂-C₄-alkylene bridge which is substituted by R₇ and

R₈;

Q is oxygen, sulfur or NR₁₀;

R₇ is hydrogen, C₁-C₄-alkoxy or C₁-C₄-alkyl;

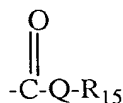
R₈ is hydrogen, C₁-C₄-alkoxy or C₁-C₄-alkyl;

5 R₉ is C₁-C₆-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl; or C₁-C₆-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl substituted by halogen or C₁-C₄-alkoxy; or phenyl, benzyl; or phenyl, benzyl substituted by C₁-C₄-alkyl, halogen, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, cyano, nitro, C₁-C₄-alkoxycarbonyl or S(O)_m-C₁-C₄-alkyl; or is C₁-C₆-alkoxyalkyl, C₁-C₆-alkylcarbonyloxyalkyl, C₁-C₆-alkoxycarbonylalkyl or C₃-C₆-cycloalkyl;

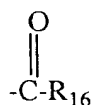
10 R₁₀ is hydrogen, C₁-C₆-alkyl, C₁-C₆-alkoxy, C₂-C₆-alkenyl, C₃-C₆-alkynyl; or C₁-C₆-alkyl, C₂-C₆-alkenyl, C₃-C₆-alkynyl substituted by halogen or C₁-C₄-alkoxy;

R₁₁ is C₁-C₆-alkyl, C₃-C₆-alkenyl, C₃-C₆-alkynyl; or C₁-C₆-alkyl, C₃-C₆-alkenyl, C₃-C₆-alkynyl substituted by halogen or C₁-C₄-alkoxy; or phenyl, benzyl; or phenyl, benzyl substituted by C₁-C₄-alkyl, halogen, haloalkyl, C₁-C₄-alkoxy, cyano, nitro, C₁-C₄-alkoxycarbonyl or S(O)_n-C₁-C₄-alkyl;

R₁₄ is hydrogen, a group



or a group



15 R₁₅ is C₁-C₆-alkyl, C₃-C₆-alkenyl, C₃-C₆-alkynyl; or C₁-C₆-alkyl, C₃-C₆-alkenyl, C₃-C₆-alkynyl substituted by halogen or C₁-C₄-alkoxy; or phenyl, benzyl; or phenyl, benzyl substituted by C₁-C₄-alkyl, halogen, haloalkyl, C₁-C₄-alkoxy, cyano, nitro, C₁-C₄-alkoxycarbonyl or S(O)_n-C₁-C₄-alkyl;

20 R₁₆ is C₁-C₆-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl; or C₁-C₆-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl substituted by halogen or C₁-C₄-alkoxy; or phenyl, benzyl; or phenyl, benzyl substituted by C₁-C₄-alkyl, halogen, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, cyano, nitro, C₁-C₄-alkoxycarbonyl or S(O)_m-C₁-C₄-alkyl; or is C₁-C₆-alkoxyalkyl, C₁-C₆-alkylcarbonyloxyalkyl, C₁-C₆-alkoxycarbonylalkyl or C₃-C₆-cycloalkyl;

25 m is 0, 1 or 2;

n is 0, 1 or 2;

p is 1 or 2;

with the proviso that R₁, R₂, R₃, R₄, X, Y and Z are not simultaneously hydrogen; and if R₁, R₃, R₄, X, Y and Z are simultaneously hydrogen, R₉ is not methyl.

2. A compound according to claim 1, in which

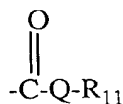
A is hydrogen, C₁-C₄-alkyl, triphenylmethyl, benzyl or a group



t is 4 or 5;

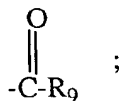
R₁ is hydrogen, fluorine or C₁-C₄-alkyl;

R₂ is hydrogen, a group



or a group

5



- R_3 is hydrogen or $\text{C}_1\text{-C}_4$ -alkyl;
 R_4 is hydrogen or $\text{C}_1\text{-C}_4$ -alkyl, or R_3 and R_4 together represent a chemical bond;
 R_5 is hydrogen, $\text{C}_1\text{-C}_4$ -alkyl, benzyl or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation;
 R_6 is hydrogen, $\text{C}_1\text{-C}_4$ -alkyl, benzyl or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation;
 X is hydrogen or $\text{C}_1\text{-C}_4$ -alkyl;
 Y is hydrogen or $\text{C}_1\text{-C}_4$ -alkyl or together with X a $-\text{CH}_2-(\text{CH}_2)_p-\text{CH}_2-$ group or together with Z a $\text{C}_1\text{-C}_4$ -alkylene bridge which is substituted by R_7 and R_8 ;
 Z is hydrogen or $\text{C}_1\text{-C}_4$ -alkyl or together with X a $\text{C}_2\text{-C}_4$ -alkylene bridge which is substituted by R_7 and R_8 ;
 Q is oxygen, sulfur or NR_{10} ;
 R_7 is hydrogen, $\text{C}_1\text{-C}_4$ -alkoxy or $\text{C}_1\text{-C}_4$ -alkyl;
 R_8 is hydrogen, $\text{C}_1\text{-C}_4$ -alkoxy or $\text{C}_1\text{-C}_4$ -alkyl;
 R_9 is $\text{C}_1\text{-C}_6$ -alkyl, $\text{C}_2\text{-C}_6$ -alkenyl, $\text{C}_2\text{-C}_6$ -alkynyl; or $\text{C}_1\text{-C}_6$ -alkyl, $\text{C}_2\text{-C}_6$ -alkenyl, $\text{C}_2\text{-C}_6$ -alkynyl substituted by halogen or $\text{C}_1\text{-C}_4$ -alkoxy; or phenyl, benzyl; or phenyl, benzyl substituted by $\text{C}_1\text{-C}_4$ -alkyl, halogen, $\text{C}_1\text{-C}_4$ -haloalkyl, $\text{C}_1\text{-C}_4$ -alkoxy, cyano, nitro, $\text{C}_1\text{-C}_4$ -alkoxycarbonyl or $\text{S}(\text{O})_m\text{-C}_1\text{-C}_4$ -alkyl;
 R_{10} is hydrogen, $\text{C}_1\text{-C}_6$ -alkyl, $\text{C}_1\text{-C}_6$ -alkoxy, $\text{C}_2\text{-C}_6$ -alkenyl, $\text{C}_3\text{-C}_6$ -alkynyl; or $\text{C}_1\text{-C}_6$ -alkyl, $\text{C}_2\text{-C}_6$ -alkenyl, $\text{C}_3\text{-C}_6$ -alkynyl substituted by halogen or $\text{C}_1\text{-C}_4$ -alkoxy;
 R_{11} is $\text{C}_1\text{-C}_6$ -alkyl, $\text{C}_3\text{-C}_6$ -alkenyl, $\text{C}_3\text{-C}_6$ -alkynyl; or $\text{C}_1\text{-C}_6$ -alkyl, $\text{C}_3\text{-C}_6$ -alkenyl, $\text{C}_3\text{-C}_6$ -alkynyl substituted by halogen or $\text{C}_1\text{-C}_4$ -alkoxy; or phenyl, benzyl; or phenyl, benzyl substituted by $\text{C}_1\text{-C}_4$ -alkyl, halogen, haloalkyl, $\text{C}_1\text{-C}_4$ -alkoxy, cyano, nitro, $\text{C}_1\text{-C}_4$ -alkoxycarbonyl or $\text{S}(\text{O})_n\text{-C}_1\text{-C}_4$ -alkyl;
 m is 0, 1 or 2;
 n is 0, 1 or 2;
 p is 1 or 2;
 with the proviso that R_1 , R_2 , R_3 , R_4 , X , Y and Z are not simultaneously hydrogen; and if R_1 , R_3 , R_4 , X , Y and Z are simultaneously hydrogen, R_9 is not methyl.

3. A compound of the formula I according to claim 1, in which
 A is hydrogen, triphenylmethyl, benzyl or a group

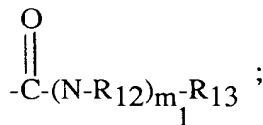
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R_2 is hydrogen or a group

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- R_{12} is hydrogen or $\text{C}_1\text{-C}_4$ -alkyl;
 m_1 is 0 or 1;
 R_{13} is $\text{C}_1\text{-C}_4$ -alkyl, methoxy, trifluoromethyl, phenyl, benzyl, phenyl substituted by halogen or methoxy; or benzyl substituted by halogen, methoxy, methylthio, cyano or trifluoromethyl.

4. A compound of the formula I according to claim 1, in which

A is hydrogen;

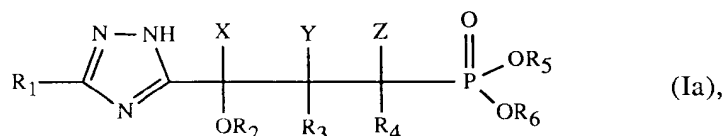
R₅ is hydrogen or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation; and

R₆ is hydrogen or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation.

5. A compound of the formula I according to claim 1, in which R₁ and A are hydrogen.

6. A compound of the formula I according to claim 1, in which R₂ and A are hydrogen.

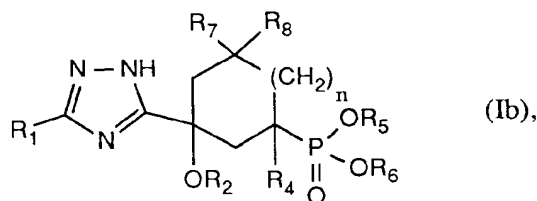
7. A compound according to claim 1 of the formula



wherein R₁, R₂, R₃, R₄, R₅, R₆, X, Y and Z have the meaning given in claim 1.

8. A compound according to claim 6, in which R₁ is hydrogen or methyl; R₂ is hydrogen or acetyl; R₃ is hydrogen or methyl; R₄ is hydrogen or methyl; R₅ is hydrogen or ethyl; R₆ is hydrogen or ethyl; X is methyl, ethyl or isopropyl; Y is hydrogen or methyl; and Z is hydrogen, methyl or ethyl.

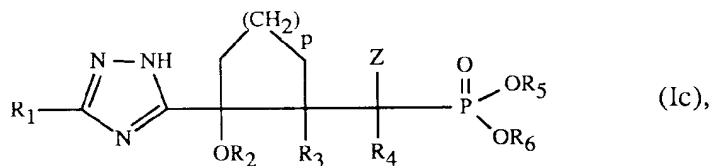
9. A compound according to claim 1 of the formula



wherein R₁, R₂, R₄, R₅, R₆, R₇ and R₈ have the meaning given in claim 1 and n is 0, 1 or 2.

10. A compound according to claim 9 in which R₁ is hydrogen or methyl; R₂ is hydrogen, acetyl or N-phenyl carbamoyl; n is 0 or 1; R₄ is hydrogen or methyl; R₅ is hydrogen, ethyl or benzyl; R₆ is hydrogen, ethyl or benzyl; R₇ is hydrogen or methyl; and R₈ is hydrogen or methyl.

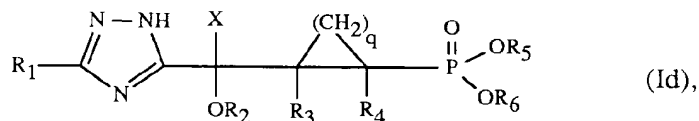
11. A compound according to claim 1 of the formula



wherein R₁, R₂, R₃, R₄, R₅, R₆, Z and p have the meaning given in claim 1.

12. A compound according to claim 11 in which R₁, R₂, R₃, R₄, R₅, R₆ and Z each is hydrogen and p is 1 or 2.

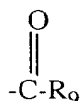
13. A compound according to claim 1 of the formula



wherein R₁, R₂, R₃, R₄, R₅, R₆ and X have the meaning given in claim 1 and q is 1, 2, 3 or 4.

14. A compound according to claim 13, wherein R₁, R₂, R₃, R₄, R₅ and R₆ each is hydrogen; X is hydrogen or methyl; and q is 1, 2, 3 or 4.

15. A compound according to claim 1, wherein A is hydrogen and R₂ is a group



16. trans-3-Hydroxy-3-(1,2,4-triazole-3-yl)-cyclohexyl-phosphonic acid according to one of claims 1, 9 and 10.

17. A herbicidal and plant-growth-inhibiting composition, which comprises one or more triazoles of the formula I according to one of claims 1 to 16.

18. A composition according to claim 17, which comprises between 0.1 % and 95 % of active substance of the formula I according to one of claims 1 to 16.

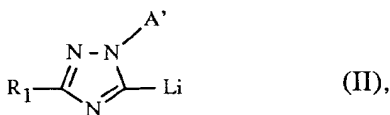
19. A method of controlling undesired plant growth, which comprises applying an effective amount of an active substance of the formula I according to one of claims 1 to 16, or a composition comprising this active substance according to claim 17, to the plants or their environment.

20. A method according to claim 19, in which an amount of active substance of between 0.005 and 2 kg is applied per hectare.

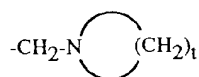
21. A method according to claim 19 for selective pre-emergence or in particular post-emergence control of weeds in crops of useful plants.

22. The use of a compound according to claim 1 or of a composition according to claim 17 for controlling undesired plant growth or for regulating plant growth.

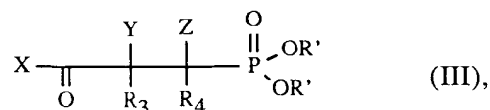
23. A process for the preparation of compounds of formula I according to claim 1, which comprises reacting a compound of the formula II



wherein A' is C₁-C₄-alkyl, C₁-C₄-alkenyl, triphenylmethyl, benzyl, a group



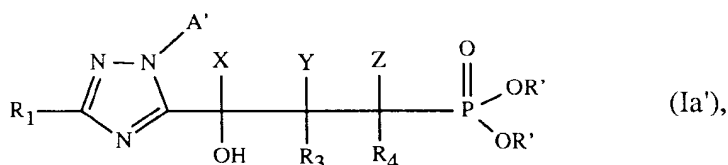
or C₁-C₄-alkyl substituted by hydroxy or C₁-C₄-alkoxy; and R₁ has the meaning given in claim 1, with aldehydes or ketones of the formula III



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wherein R_3 , R_4 , X , Y and Z have the meaning given in claim 1 and R' is C_1 - C_4 alkyl or benzyl, to give a compound of the formula Ia'

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wherein A' and R_1 , R_3 , R_4 , X , Y and Z have the meaning given in claim 1 and A' and R' have the meanings given in formulae II and III, and optionally cleaving protecting groups A' and/or R' and further converting them into a salt.

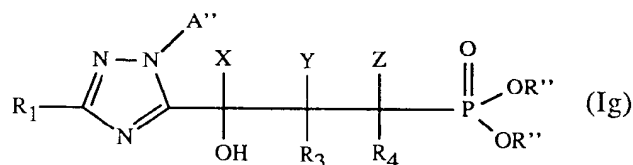
24. A process according to claim 23 which comprises cleavage of protecting groups for A as triphenylmethylgroup;

25

R_5 as C_1 - C_4 alkyl, benzyl or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation; and

R_6 as C_1 - C_4 alkyl, benzyl or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation which comprises reacting sequentially or in a one step process the compound of formula

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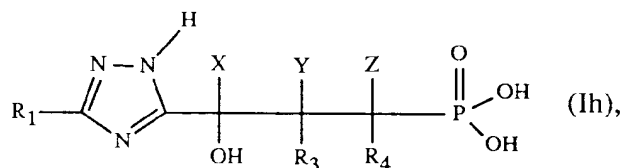


35

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wherein R_1 , R_3 , R_4 , X , Y and Z have the meaning given in claim 1 and A'' is triphenylmethyl and R'' is C_1 - C_4 alkyl, benzyl or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation, with an organic or inorganic acid to give the compound of the formula

45

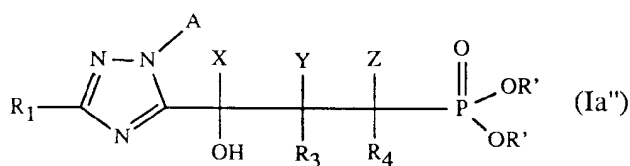


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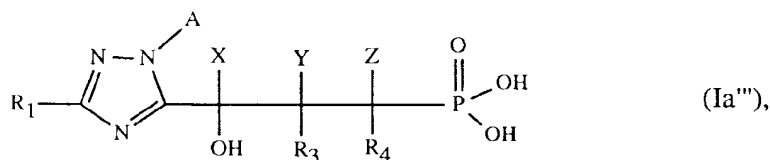
wherein R_1 , R_3 , R_4 , X , Y and Z have the meaning given in claim 1.

55

25. A process for the preparation of compounds of the formula I according to claim 1, wherein R_5 and R_6 are hydrogen, which comprises treating a compound of formula Ia''

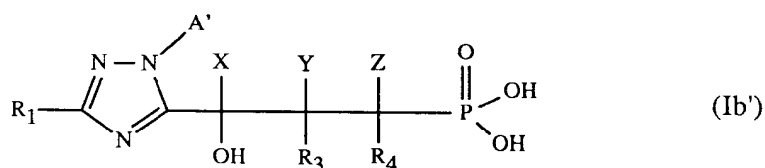


10 with an acid or a halosilane to obtain a compound of the formula Ia'''

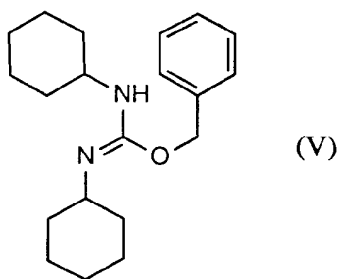


20 wherein A, R₁, R₃, R₄, X, Y and Z have the meaning given in claim 1 and R' has the meaning given in claim 23.

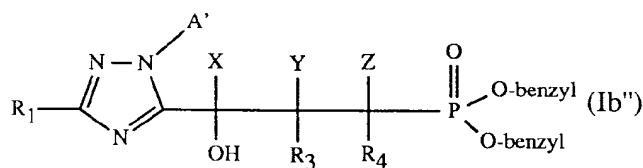
25 **26.** A process for the preparation of compounds of the formula I, wherein R₅ and R₆ are benzyl which comprises reacting the free phosphonic acid compound Ib'



35 wherein R₁, R₃, R₄, X, Y and Z have the meaning given in claim 1 and A' has the meaning given in claim 23, with 2 equivalents of O-benzyl-N,N'-dicyclohexylisourea of the formula V

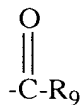


45 to give the compound of the formula Ib''

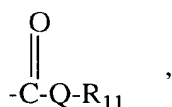


55 wherein R₁, R₃, R₄, X, Y and Z have the meaning given in claim 1 and A' has the meaning given in claim 23.

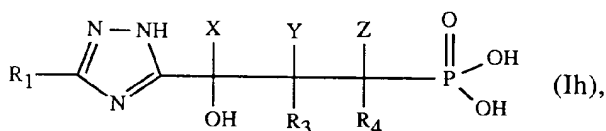
27. A process for the preparation of compounds of the formula I, wherein R_2 is a group



or a group

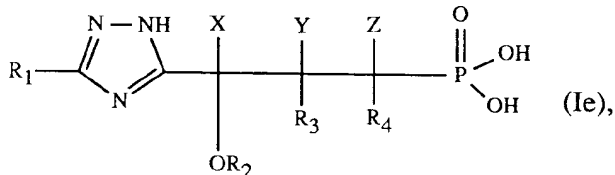


which comprises reacting a compound of formula Ih



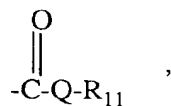
with acid halides or anhydrides of the formula

$\text{R}_9\text{-CO-}(\text{halogen, especially chlorine})$ or $\text{R}_{11}\text{-Q-CO-}(\text{halogen, especially chlorine})$ or $(\text{R}_9\text{CO})_2\text{O}$ to give the compound of the formula

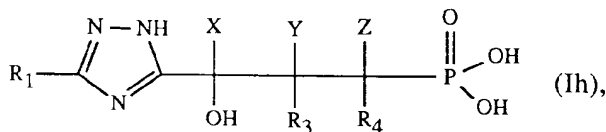


wherein R_1 , R_3 , R_4 , R_9 , R_{11} , Q , X , Y and Z have the meaning given in claim 1 and R_2 has the meaning given in claim 1 except for hydrogen.

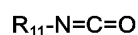
28. A process according to claim 23 for the preparation of compounds of formula I, wherein R_2 is a group



in which Q is NR_{10} and R_{10} is hydrogen, which comprises reacting a compound of formula Ih



with isocyanates of the formula





Claims for the following Contracting State : Sp

- 15



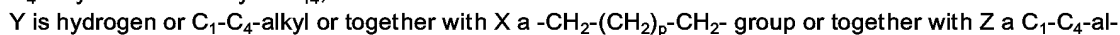
25 A is hydrogen, C₁-C₄-alkyl, C₁-C₄-alkenyl, triphenylmethyl, benzyl, a group



R₂ is hydrogen, a group



45



kylene bridge which is substituted by R₇ and R₈;

Z is hydrogen or C₁-C₄-alkyl or together with X a C₂-C₄-alkylene bridge which is substituted by R₇ and R₈;

Q is oxygen, sulfur or NR₁₀;

R₇ is hydrogen, C₁-C₄-alkoxy or C₁-C₄-alkyl;

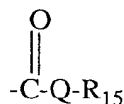
R₈ is hydrogen, C₁-C₄-alkoxy or C₁-C₄-alkyl;

R₉ is C₁-C₆-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl; or C₁-C₆-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl substituted by halogen or C₁-C₄-alkoxy; or phenyl, benzyl; or phenyl, benzyl substituted by C₁-C₄-alkyl, halogen, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, cyano, nitro, C₁-C₄-alkoxycarbonyl or S(O)_m-C₁-C₄-alkyl; or is C₁-C₆-alkoxyalkyl, C₁-C₆-alkylcarbonyloxyalkyl, C₁-C₆-alkoxycarbonylalkyl or C₃-C₆-cycloalkyl;

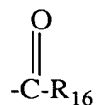
R₁₀ is hydrogen, C₁-C₆-alkyl, C₁-C₆-alkoxy, C₂-C₆-alkenyl, C₃-C₆-alkynyl; or C₁-C₆-alkyl, C₂-C₆-alkenyl, C₃-C₆-alkynyl substituted by halogen or C₁-C₄-alkoxy;

R₁₁ is C₁-C₆-alkyl, C₃-C₆-alkenyl, C₃-C₆-alkynyl; or C₁-C₆-alkyl, C₃-C₆-alkenyl, C₃-C₆-alkynyl substituted by halogen or C₁-C₄-alkoxy; or phenyl, benzyl; or phenyl, benzyl substituted by C₁-C₄-alkyl, halogen, haloalkyl, C₁-C₄-alkoxy, cyano, nitro, C₁-C₄-alkoxycarbonyl or S(O)_n-C₁-C₄-alkyl;

R₁₄ is hydrogen, a group



or a group



R₁₅ is C₁-C₆-alkyl, C₃-C₆-alkenyl, C₃-C₆-alkynyl; or C₁-C₆-alkyl, C₃-C₆-alkenyl, C₃-C₆-alkynyl substituted by halogen or C₁-C₄-alkoxy; or phenyl, benzyl; or phenyl, benzyl substituted by C₁-C₄-alkyl, halogen, haloalkyl, C₁-C₄-alkoxy, cyano, nitro, C₁-C₄-alkoxycarbonyl or S(O)_n-C₁-C₄-alkyl;

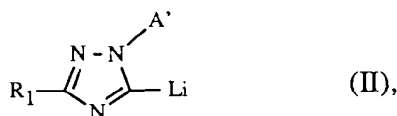
R₁₆ is C₁-C₆-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl; or C₁-C₆-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl substituted by halogen or C₁-C₄-alkoxy; or phenyl, benzyl; or phenyl, benzyl substituted by C₁-C₄-alkyl, halogen, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, cyano, nitro, C₁-C₄-alkoxycarbonyl or S(O)_m-C₁-C₄-alkyl; or is C₁-C₆-alkoxyalkyl, C₁-C₆-alkylcarbonyloxyalkyl, C₁-C₆-alkoxycarbonylalkyl or C₃-C₆-cycloalkyl;

m is 0, 1 or 2;

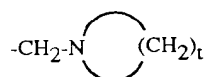
n is 0, 1 or 2;

p is 1 or 2;

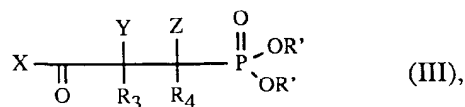
with the proviso that R₁, R₂, R₃, R₄, X, Y and Z are not simultaneously hydrogen; and if R₁, R₃, R₄, X, Y and Z are simultaneously hydrogen, R₉ is not methyl; which comprises reacting a compound of the formula II



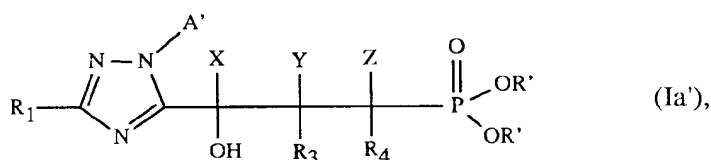
wherein A' is C₁-C₄-alkyl, C₁-C₄-alkenyl, triphenylmethyl, benzyl, a group



or C₁-C₄-alkyl substituted by hydroxy or C₁-C₄-alkoxy; and R₁ has the meaning given in formula I, with aldehydes or ketones of the formula III



wherein R₃, R₄, X, Y and Z have the meaning given in formula I and R' is C₁-C₄alkyl or benzyl, to give a compound of the formula Ia'

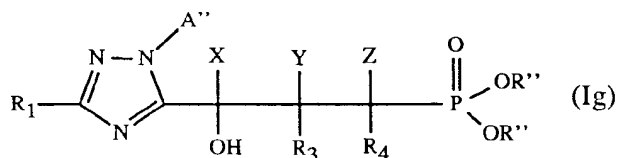


wherein A' and R₁, R₃, R₄, X, Y and Z have the meaning given above and A' and R' have the meanings given in formulae II and III, and optionally cleaving protecting groups A' and/or R' and further converting them into a salt.

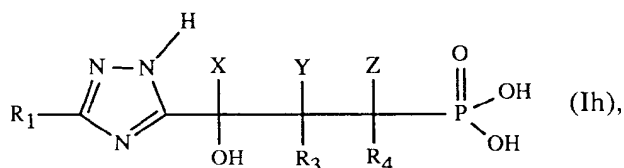
2. A process according to claim 1 which comprises cleavage of protecting groups for A as triphenylmethylgroup;

R₅ as C₁-C₄-alkyl, benzyl or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation; and

R₆ as C₁-C₄-alkyl, benzyl or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation which comprises reacting sequentially or in a one step process the compound of formula

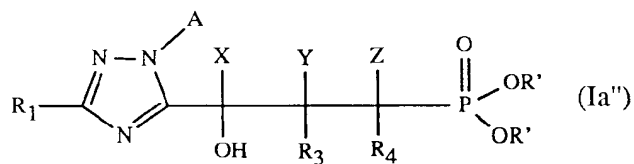


wherein R₁, R₃, R₄, X, Y and Z have the meaning given in claim 1 and A'' is triphenylmethyl and R'' is C₁-C₄-alkyl, benzyl or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation, with an organic or inorganic acid to give the compound of the formula

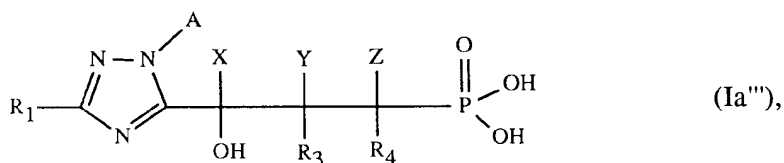


wherein R₁, R₃, R₄, X, Y and Z have the meaning given in claim 1.

3. A process for the preparation of compounds of the formula I according to claim 1, wherein R₅ and R₆ are hydrogen, which comprises treating a compound of formula Ia''

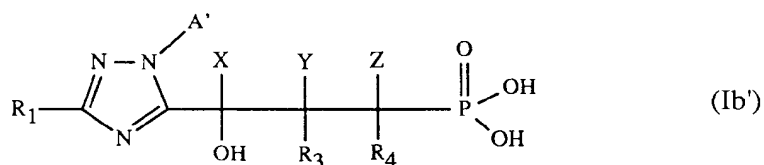


10 with an acid or a halosilane to obtain a compound of the formula Ia'''

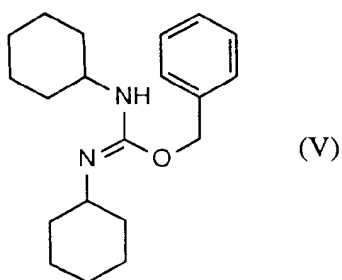


20 wherein A, R₁, R₃, R₄, X, Y, R' and Z have the meaning given in claim 1.

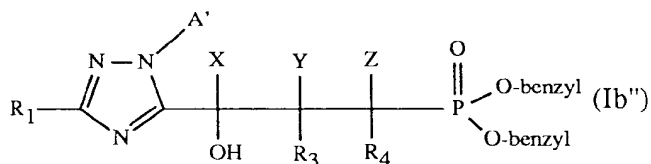
4. A process for the preparation of compounds of the formula I, wherein R₅ and R₆ are benzyl which comprises reacting the free phosphonic acid compound Ib'



30 wherein R₁, R₃, R₄, X, Y, R' and Z have the meaning given in claim 1, with 2 equivalents of O-benzyl-N,N'-dicyclohexylisourea of the formula V

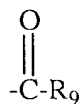


45 to give the compound of the formula Ib''



55 wherein R₁, R₃, R₄, X, Y, A' and Z have the meaning given in claim 1.

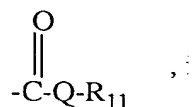
5. A process for the preparation of compounds of the formula I, wherein R₂ is a group



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or a group

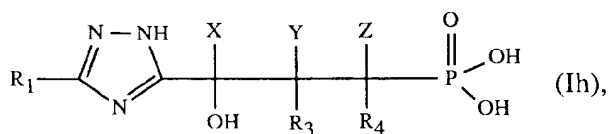
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which comprises reacting a compound of formula Ih

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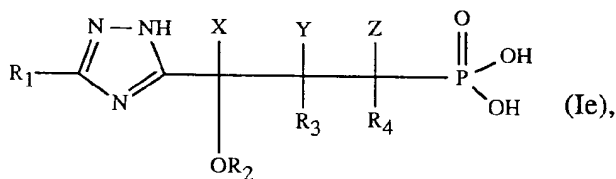


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with acid halides or anhydrides of the formula

 $\text{R}_9\text{-CO-(halogen, especially chlorine) or R}_{11}\text{-Q-CO-(halogen, especially chlorine) or (R}_9\text{CO)}_2\text{O}$ to give the compound of the formula

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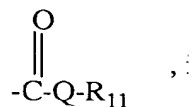
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wherein R_1 , R_3 , R_4 , R_9 , R_{11} , Q , X , Y and Z have the meaning given in claim 1 and R_2 has the meaning given in claim 1 except for hydrogen.

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6. A process according to claim 1 for the preparation of compounds of formula I, wherein R_2 is a group

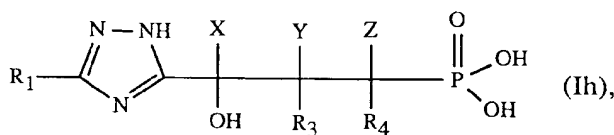
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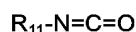
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in which Q is NR_{10} and R_{10} is hydrogen, which comprises reacting a compound of formula Ih

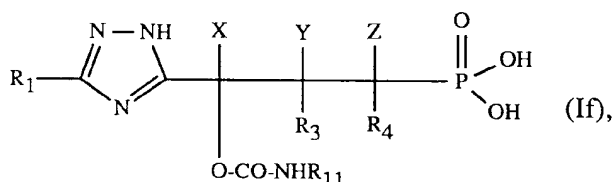
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with isocyanates of the formula



to give the carbamates of the formula



wherein R_1 , R_3 , R_4 , R_{11} , X, Y and Z have the meaning given in claim 1.

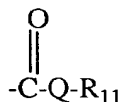
7. A process according to claim 1 for the preparation of compounds of formula I, wherein A is hydrogen, C_1 - C_4 -alkyl, triphenylmethyl, benzyl or a group



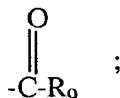
t is 4 or 5;

R_1 is hydrogen, fluorine or C_1 - C_4 -alkyl;

R_2 is hydrogen, a group



or a group



R_3 is hydrogen or C_1 - C_4 -alkyl;

R_4 is hydrogen or C_1 - C_4 -alkyl, or R_3 and R_4 together represent a chemical bond;

R_5 is hydrogen, C_1 - C_4 -alkyl, benzyl or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation;

R_6 is hydrogen, C_1 - C_4 -alkyl, benzyl or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation;

X is hydrogen or C_1 - C_4 -alkyl;

Y is hydrogen or C_1 - C_4 -alkyl or together with X a $-\text{CH}_2-(\text{CH}_2)_p-\text{CH}_2-$ group or together with Z a C_1 - C_4 -alkylene bridge which is substituted by R_7 and R_8 ;

Z is hydrogen or C_1 - C_4 -alkyl or together with X a C_2 - C_4 -alkylene bridge which is substituted by R_7 and R_8 ;

Q is oxygen, sulfur or NR_{10} ;

R_7 is hydrogen, C_1 - C_4 -alkoxy or C_1 - C_4 -alkyl;

R_8 is hydrogen, C_1 - C_4 -alkoxy or C_1 - C_4 -alkyl;

R_9 is C_1 - C_6 -alkyl, C_2 - C_6 -alkenyl, C_2 - C_6 -alkynyl; or C_1 - C_6 -alkyl, C_2 - C_6 -alkenyl, C_2 - C_6 -alkynyl substituted by halogen or C_1 - C_4 -alkoxy; or phenyl, benzyl; or phenyl, benzyl substituted by C_1 - C_4 -alkyl, halogen, C_1 - C_4 -haloalkyl, C_1 - C_4 -alkoxy, cyano, nitro, C_1 - C_4 -alkoxycarbonyl or $\text{S}(\text{O})_m$ - C_1 - C_4 -alkyl;

R_{10} is hydrogen, C_1 - C_6 -alkyl, C_1 - C_6 -alkoxy, C_2 - C_6 -alkenyl, C_3 - C_6 -alkynyl; or C_1 - C_6 -alkyl, C_2 - C_6 -alkenyl, C_3 - C_6 -alkynyl substituted by halogen or C_1 - C_4 -alkoxy;

R_{11} is C_1 - C_6 -alkyl, C_3 - C_6 -alkenyl, C_3 - C_6 -alkynyl; or C_1 - C_6 -alkyl, C_3 - C_6 -alkenyl, C_3 - C_6 -alkynyl substituted

by halogen or C₁-C₄-alkoxy; or phenyl, benzyl; or phenyl, benzyl substituted by C₁-C₄-alkyl, halogen, halomethyl, C₁-C₄-alkoxy, cyano, nitro, C₁-C₄-alkoxycarbonyl or S(O)_n-C₁-C₄-alkyl;

m is 0, 1 or 2;

n is 0, 1 or 2;

p is 1 or 2;

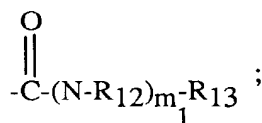
with the proviso that R₁, R₂, R₃, R₄, X, Y and Z are not simultaneously hydrogen; and if R₁, R₃, R₄, X, Y and Z are simultaneously hydrogen, R₉ is not methyl.

8. A process according to claim 1 for the preparation of compounds of formula I, wherein

A is hydrogen, triphenylmethyl, benzyl or a group



R₂ is hydrogen or a group



R₁₂ is hydrogen or C₁-C₄-alkyl;

m₁ is 0 or 1;

R₁₃ is C₁-C₄-alkyl, methoxy, trifluoromethyl, phenyl, benzyl, phenyl substituted by halogen or methoxy; or benzyl substituted by halogen, methoxy, methylthio, cyano or trifluoromethyl.

9. A process according to claim 1 for the preparation of compounds of formula I, wherein

A is hydrogen;

R₅ is hydrogen or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation; and

R₆ is hydrogen or an alkali metal, alkaline earth metal, ammonium, organic ammonium, trialkylsulphonium, trialkylsulfoxonium, phosphonium or amidinium cation.

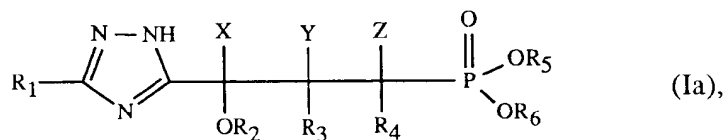
10. A process according to claim 1 for the preparation of compounds of formula I, wherein

R₁ and A are hydrogen.

11. A process according to claim 1 for the preparation of compounds of formula I, wherein

R₂ and A are hydrogen.

12. A process according to claim 1 for the preparation of compounds of formula Ia,



wherein R₁, R₂, R₃, R₄, R₅, R₆, X, Y and Z have the meaning given in claim 1.

13. A process according to claim 11 for the preparation of compounds of formula I,

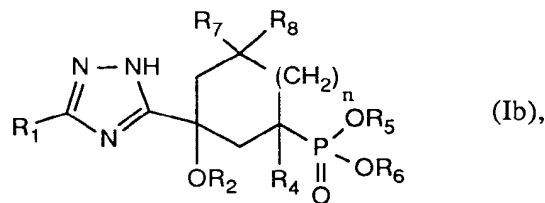
wherein

R₁ is hydrogen or methyl; R₂ is hydrogen or acetyl; R₃ is hydrogen or methyl; R₄ is hydrogen or methyl;

R₅ is hydrogen or ethyl; R₆ is hydrogen or ethyl; X is methyl, ethyl or isopropyl; Y is hydrogen or methyl;

and Z is hydrogen, methyl or ethyl.

14. A process according to claim 1 for the preparation of compounds of the formula

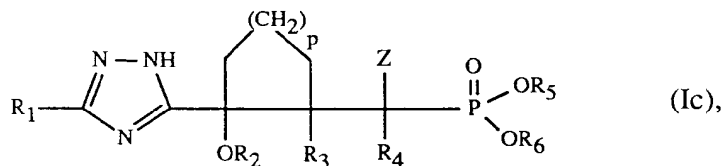


10 wherein R_1 , R_2 , R_4 , R_5 , R_6 , R_7 and R_8 have the meaning given in claim 1 and n is 0, 1 or 2.

- 15 **15.** A process according to claim 14 for the preparation of compounds of formula Ib, wherein

R_1 is hydrogen or methyl; R_2 is hydrogen, acetyl or N-phenyl carbamoyl; n is 0 or 1; R_4 is hydrogen or methyl; R_5 is hydrogen, ethyl or benzyl; R_6 is hydrogen, ethyl or benzyl; R_7 is hydrogen or methyl; and R_8 is hydrogen or methyl.

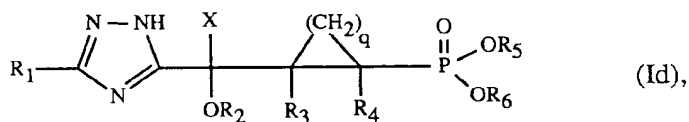
- 16.** A process according to claim 1 for the preparation of compounds of formula



25 wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , Z and p have the meaning given in claim 1.

- 17.** A process according to claim 16 for the preparation of compounds of formula Ic, wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 and Z each is hydrogen and p is 1 or 2.

- 30 **18.** A process according to claim 1 for the preparation of compounds of the formula



wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 and X have the meaning given in claim 1 and q is 1, 2, 3 or 4.

- 40 **19.** A process according to claim 18 for the preparation of compounds of formula Id, wherein R_1 , R_2 , R_3 , R_4 , R_5 and R_6 each is hydrogen; X is hydrogen or methyl; and q is 1, 2, 3 or 4.

- 20.** A process according to claim 1 for the preparation of compounds of formula I, wherein A is hydrogen and R_2 is a group



- 21.** A process according to claim 1 for the preparation of compound trans-3-Hydroxy-3-(1,2,4-triazole-3-yl)-cyclohexyl-phosphonic acid.

- 55 **22.** A herbicidal and plant-growth-inhibiting composition, which comprises one or more triazoles of the formula I according to claim 1.

- 23.** A composition according to claim 22, which comprises between 0.1 % and 95 % of active substance of the formula I according to claim 1.

24. A method of controlling undesired plant growth, which comprises applying an effective amount of an active substance of the formula I according to claim 1, or a composition comprising this active substance according to claim 22, to the plants or their environment.

5 **25.** A method according to claim 24, in which an amount of active substance of between 0.005 and 2 kg is applied per hectare.

26. A method according to claim 25 for selective pre-emergence or in particular post-emergence control of weeds in crops of useful plants.

10 **27.** The use of a compound according to claim 1 or of a composition according to claim 22 for controlling undesired plant growth or for regulating plant growth.

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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 81 0596

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,A	EP-A-0 078 613 (IMPERIAL CHEMICAL INDUSTRIES PLC) * the whole document *	1,17-22	C07F9/6518 A01N57/24
A	EP-A-0 065 216 (HOECHST A.G.) * the whole document *	1,17-22	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C07F A01N
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 19 NOVEMBER 1992	Examiner BESLIER L.M.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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